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EXCITED STATE WAVE FUNCTIONS BY CONFIGURATION INTERACTION

by

© WILLIAM DEN HERTOG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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OF MASTER OF SCIENCE

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled EXCITED STATE WAVE FUNCTIONS BY CONFIGURATION INTERACTION submitted by William den Hertog in partial fulfilment of the requirements for the degree of Master of Science.

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Supervisor

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Date: August 9 1973

... all things by fire consumed ablaze,
Within their frame lay up, if naught besides,
At least those atoms whence derives their power
To throw forth fire and send out light from under,
To shoot the sparks and scatter embers wide.

LUCRETIUS,

Of the Nature of Things, 1st Century B.C.

(translation by William Ellery Leonard, 1916)

ABSTRACT

The problem of obtaining wave functions and energy bounds is treated in this work within the context of the configuration interaction (CI) method. Two distinct methods in obtaining the CI function ϕ_k for the k^{th} state, ψ_k with true energy W_k, are investigated: (1) simultaneous minimization of the "energy error" $\epsilon_k = \langle \phi_k | H - W_k | \phi_k \rangle$ and of ϵ_k^2/Δ_k with the "local energy error" $\Delta_k = \langle \phi_k | (H - W_k)^2 | \phi_k \rangle$ and (2) minimization of ϵ_k above by the Rayleigh-Ritz method.

The first method is found not to give dependable numerical bounds to the deviation of ϕ_k from ψ_k and a new analysis of the reason for this is discussed. Thus the major emphasis of the work is upon the usefulness of the Rayleigh-Ritz method in obtaining excited state wave functions and upper bounds to energies. It is shown that the results thus obtained for two-electron ground states very closely satisfy the criteria of the first method.

The group of states chosen for this model investigation is that of the ^{1}S states of helium. A systematic search for a decent CI basis has culminated in the production of a set of CI functions for these states with energies within 0.003 to 0.005 a.u. of the corresponding true state energies. Shortly after the completion of this work superficially similar results were published

but the basis used there introduces errors which are not present in the results reported here. Thus the 1sns ^1S state functions and energies obtained in the present work are not only the most dependable yet obtained by the Rayleigh-Ritz method, but also show the promise of the method for obtaining excited state wave functions.

The present work stimulated the development, by Birss, of the "rational orbital" analysis, which is similar to the well established natural orbital analysis but reflects the relative spatial concentration of the two electrons in the states treated in this work. The analysis is presented as used here for the first time. The expected decrease in importance of correlation and approach of the inner electron function to a He^+ 1s wave function upon consideration of progressively higher excited states is placed upon a firm numerical basis by the analysis.

A principle is established for constructing a CI basis for doubly excited ^1S state functions. Such a basis must be formed from configuration functions spanning a maximal part of the space of 1sns ^1S state functions as well as from configuration functions lying as much as possible in the space of 2sns ^1S state functions. The first criterion is met by the configurations developed for the 1sns ^1S states. A judicious choice of configurations,

satisfying the second criterion, has led to a CI function for the $(2s)^2\ ^1S$ state which places the energy of the state between -0.730 and -0.734 a.u.

On this basis the assignment of the $(2s)^2\ ^1S$ - $1s2s\ ^1S$ transition to a corona line of frequency 279,715 cm^{-1} (Krüger, 1930) is rejected. A similar rejection (Holoien, 1958) is shown to have been made on an untenable basis.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to Prof. Dr. F. W. Birss for his generous giving of his expertise and his time during the course of this work. I shall be forever the richer for having experienced his scholarly approach to matters scientific. The intellectually stimulating sessions with Prof. Birss will be remembered with nostalgia.

Special appreciation and sincere thanks are extended to Prof. Dr. S. Huzinaga for his most helpful suggestions and his kind interest in my work.

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I. Theory of Variational Methods

I.1 Introduction

It is well known that the time-independent, non-relativistic Schroedinger equation of free atoms or ions with two or more electrons defies exact solution. In the method of configuration interaction, applied in the work to be reported, an approximation to the exact solution consists of a trial function constructed on the principles of vector algebra and the calculus of variation. The function is set up as a linear expansion of a selection of basis functions expected to best span the space containing the exact solution aimed for. A functional of the trial function is chosen to serve as a criterion of goodness of the function. The latter is improved by optimizing the expansion coefficients and parameters of the basis functions to obtain a stationary value for the functional as close as possible to the exact value known by experiment or theoretical prediction.

In the subject of this thesis there are two functionals of main concern. With the Schroedinger equation written as

$$H\Psi_k = W_k\Psi_k,$$

in which $k = 0$ refers to the ground state and $k > 0$ refers

to the k^{th} excited state of a certain symmetry, and with a trial function to approximate Ψ_k denoted by Φ_k, these functionals are defined by:

$$E_k = \langle \Phi_k | H | \Phi_k \rangle$$

$$\tilde{\Delta}_k = \langle \Phi_k | (H-W_k)^2 | \Phi_k \rangle$$

They define:

$$\varepsilon_k = (E_k - W_k)$$

and

$$\varepsilon_k^2 / \tilde{\Delta}_k$$

The definitions imply that ε_k and $\tilde{\Delta}_k \to 0$ as $\Phi_k \to \Psi_k$.

The thesis reports on the study of two different variational methods to construct excited state wave functions. The methods are based on:

1. The minimization of ε_k
2. The simultaneous minimization of $\varepsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$.

I.2 The Minimization of ε_k

The configuration interaction method, applied in this work, is the Rayleigh-Ritz variational procedure in which the basis functions are symmetry adapted two-electron configurations. The method, mainly applied to ground,

states, owes its usefulness to the fact that the addition of configurations in the trial function is equivalent to approaching the use of a complete basis set.

For the application to excited states the MacDonald theorem is of central importance (1). Applied to the CI method it establishes that the m^{th} lowest eigenvalue obtained from any given basis set of N symmetry adapted configurations is an upper bound of the exact m^{th} lowest energy of the states of the symmetry under consideration.

Clearly the theorem immediately provides a variational criterion, namely the minimization of $\varepsilon_k = E_k - W_k$ or of E_k if the exact energy of the k^{th} excited state is not known. Yet, while the theorem was established as long as some thirty years ago, and since has been occasionally referred to in the texts and literature (2,3,4,5), no application to excited states was found in the literature at the time that the work for the thesis was undertaken.

An explanation of this unexplored opportunity is difficult to give. It may lie in the fact that in the large amount of ground state work done, the linear variations to obtain the lowest E_o value at the same time would yield a set of E_k values invariably too high to be of any use as upper bounds. For example, the basis set used by Weiss (4) generates for helium in the same minimization a ground state energy of -2.90270 a.u. (accurate

value : -2.90372 a.u. [Table 14]) and an upper bound of -1.86246 a.u. to the exact energy of -2.14595 a.u. of the first ^1S excited state. This may have led to a general impression that the MacDonald theorem was not of much practical value, although in that case it must have been overlooked that a basis set of configurations good for a ground state must, of course, be expected to be a poor one for excited states.

The judicious choice of a particular basis set is crucial if the MacDonald theorem is to be applied to excited states. Indeed this consideration has been the starting point of the work to be reported below. Several aspects have been explored such as different types of orbital functions in the basis configurations, the size of the basis sets in relation to the problem of convergence towards the exact energy, the role of the linear (expansion coefficients) and non-linear (orbital exponents) variational parameters, and the selection of the configurations.

These studies have led to the computation of a set of ^1S states of helium with energies sufficiently close to the exact ones to demonstrate the strong potential of the Rayleigh-Ritz variational method for excited states.

I.3 The Simultaneous Minimization of $\epsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$

A method which uses the functionals $\tilde{\Delta}_k$ and $\epsilon_k^2/\tilde{\Delta}_k$ as variational criteria has recently been proposed by Messmer (6) and modified by Choi, Lebeda and Messmer (7). The method is presented as a better alternative to minimizing either ϵ_k or $\tilde{\Delta}_k$ alone. It had been shown (13,14) that in the latter minimizations wave functions are obtained which have minimum errors in certain regions of configuration space, rather than over the whole of configuration space. On the one hand in minimizing $\tilde{\Delta}_k$ the errors in the wave function associated with the closeness of the electrons will be minimized; in this connection $\tilde{\Delta}$ is called the "local energy error" (13), representing with reference to the closeness of the electrons, "short range errors." On the other hand, "long range errors" are minimized by minimizing ϵ_k, the "energy error" (13,14). In this case the wave functions obtained should be suitable for describing properties such as the radial density or diamagnetic susceptibility where long range errors are important.

The basic premise of Messmer's proposal is that the best approximation to the exact wave function Ψ_k is the trial function ϕ_k which has the maximum overlap a_k with Ψ_k as defined by $a_k = \langle \phi_k | \Psi_k \rangle$. He shows that maximizing a_k is equivalent to obtaining the smallest root-mean-

square deviation of ϕ_k from Ψ_k, which implies that the error of ϕ_k over the whole of configuration space is minimized. It is then shown that the trial function with maximum overlap must be that ϕ_k which gives ϵ_k^2/Δ_k its stationary value. In the minimization of ϵ_k^2/Δ_k a restriction is introduced (7): in the variational procedure to be applied both ϵ_k^2/Δ_k and Δ_k should simultaneously tend towards minima. For this reason the proposed minimizations are presented as an alternative to separate minimization of ϵ_k or Δ_k.

Unfortunately the goodness of ϕ_k cannot be assessed by the very criterion the method is based upon, namely that of maximum overlap a_k. The overlap $a_k = \langle \phi_k | \Psi_k \rangle$ cannot be calculated since the problem is precisely that Ψ_k is not known. For this reason Choi et al (7) derived upper and lower bounds to a_k which were to serve instead of a_k as criteria for assessing ϕ_k obtained by ϵ_k^2/Δ_k and Δ_k minimization.

These bounds were indirectly expressed in terms of a function which defines the deviation of the trial function from the true wave function. Since the exact eigen states $\{\Psi_n\}$ of a defined symmetry form a complete set, one can write the trial function as:

$$\phi_k = \sum_n^{\infty} a_n \Psi_n = a_k \Psi_k + \sum_{n \neq k}^{\infty} a_n \Psi_n$$

The term $\sum_{n\neq k}^{\infty} a_n \Psi_n$ is now replaced by a weighted deviation function $\Psi_{\chi,k}$:

$$\Phi_k = a_k \Psi_k + a_{\chi,k} \Phi_{\chi,k}$$

Normalization ensures that:

$$\langle \Phi_k | \Phi_k \rangle = \langle \Psi_k | \Psi_k \rangle = \langle \Phi_{\chi,k} | \Phi_{\chi,k} \rangle = 1$$

and it follows that

$$\langle \Psi_k | \Phi_{\chi,k} \rangle = 0$$

and

$$a_k^2 + a_{\chi,k}^2 = 1.$$

The last equation establishes the relation between the upper and lower bounds of a_k, the overlap, on the one hand and the lower and upper bounds of $a_{\chi,k}$, the deviation coefficient, on the other hand.

Choi et al derived the following bounds for $a_{\chi,k}^2$:

$$\frac{\epsilon_k^2}{\Delta_k} \leq a_{\chi,k}^2 \leq \frac{\Delta_k}{(W_k' - W_k)^2},$$

in which W_k' is, in the exact energy spectrum, the value closest to W_k. It is assumed that both W_k' and W_k are known, either by computation or by measurement. The

expression above illustrates how simultaneous minimization of $\epsilon_k^2/\bar{\Delta}_k$ and $\bar{\Delta}_k$ should diminish the deviation coefficient as well as narrow its range, thereby yielding a trial function ϕ_k with maximum a_k. It is evident that the usefulness of the method then depends entirely on the goodness of the proposed bounds. Even if a good ϕ_k would be obtained, its goodness can only be established if the bounds enclose a narrow range for the corresponding a_χ^2.

It is this point which requires closer consideration. Some work had been done which strictly as numerical evidence has thrown serious doubt on the goodness of the upper bound $\bar{\Delta}_k/(W_k' - W_k)^2$. The first is the same publication which proposed the bounds (7). There a numerical example of the method is given in an application to the harmonic oscillator. Upper and lower bounds are calculated for various trial wave functions for the 5^{th} and 7^{th} excited states. The results for the lowest obtained values for a_χ^2 are presented here.

Excited State	Lower Bound	a_χ^2	Upper Bound
5^{th}	8.274×10^{-10}	8.290×10^{-10}	2.971×10^{-8}
7^{th}	3.959×10^{-6}	3.985×10^{-6}	6.290×10^{-5}

The authors had good reason to state that the upper bounds are "not as satisfactory" as the lower bounds.

Indeed if all values are expressed relative to $a_\chi^2 = 1$ one obtains

Excited State	Lower Bound	a_χ^2	Upper Bound
5^{th}	0.998	1	36
7^{th}	0.994	1	16

Further indications that the upper bounds are suspect came from Liebe (8) in his applications of the method to the calculations of SCF wave functions for, among others, eleven excited states of helium, three excited states of lithium and the ground states of helium, lithium, beryllium and carbon. He found that "in all cases the value of $\epsilon^2/\tilde{\Delta}$ could be reduced to 0.01 or less, whereas the $\tilde{\Delta}/(W_k' - W_k)^2$ value was of the order of 100 to 200."

Choi et al do not go further than stating that the upper bounds are not as good as the lower bounds; Liebe expresses the belief that "this inability to reduce the upper bounds of a_χ^2 reasonably is connected with the orbital expansion SCF approach." But it was felt by this author that a close examination of the derivation itself of the upper bound was in order. This examination has uncovered a fundamental weakness in the derivation

which does make $\tilde{\Delta}_k/(W'_k - W_k)^2$ a poor upper bound indeed.

To expose this weakness it is not necessary to reproduce the complete derivation given by Choi et al. It will suffice to summarize here the pertinent definitions and derived equations.

Definitions:

In terms of the eigen functions Ψ_i of the Schroedinger equation

$$H \Psi_n = W_n \Psi_n$$

the trial function Φ_k for the k^{th} excited state is written as:

$$\Phi_k = \sum_n a_n \Psi_n = a_k \Psi_k + \sum_{n \neq k} a_n \Psi_n$$

A deviation function $\Phi_{\chi,k}$ and deviation coefficient $a_{\chi,k}$ are introduced by:

$$\sum_{n \neq k} a_n \Psi_n = a_{\chi,k} \Phi_{\chi,k}$$

so that

$$\Phi_k = a_k \Psi_k + a_{\chi,k} \Phi_{\chi,k}$$

with

$$a_k^2 + a_{\chi,k}^2 = 1$$

An energy error ε_k is defined by

$$E_k = \langle \Phi_k | H | \Phi_k \rangle$$

$$W_k = \langle \Psi_k | H | \Psi_k \rangle$$

$$\varepsilon_k = E_k - W_k$$

and the functionals $\tilde{\Delta}_k$ and $\tilde{\Delta}_{\chi,k}$ are:

$$\tilde{\Delta}_k = \langle \Phi_k | (H - W_k)^2 | \Phi_k \rangle$$

$$\tilde{\Delta}_{\chi,k} = \langle \Phi_{\chi,k} | (H - W_k)^2 | \Phi_{\chi,k} \rangle$$

The constraints are:

$$\langle \Phi_k | \Phi_k \rangle = \langle \Psi_k | \Psi_k \rangle = \langle \Phi_\chi | \Phi_\chi \rangle = 1$$

and

$$\langle \Psi_k | \Phi_\chi \rangle = 0.$$

Equations derived from above definitions:

$$a_{\chi,k}^2 = \sum_{n \neq k} a_n^2 \tag{1}$$

$$\tilde{\Delta}_k = \sum_n a_n^2 (W_n - W_k)^2 \tag{2}$$

$$\tilde{\Delta}_{\chi,k} = \frac{\sum_{n \neq k} a_n^2 (W_n - W_k)^2}{a_{\chi,k}^2} \tag{3}$$

These three equations lead to

$$a^2_{\chi,k} = \frac{\tilde{\Delta}_k}{\tilde{\Delta}_{\chi,k}} \qquad (4)$$

Choi et al then introduce the inequality

$$\sum_{n\neq k} a_n^2 \, (W_m - W_k)^2 \geq \sum_{n\neq k} a_n^2 \, (W'_k - W_k)^2 \qquad (5)$$

which holds by the definition of W'_k as the value closest to W_k in the energy spectrum. This inequality combines with equation (3) to:

$$\tilde{\Delta}_{\chi,k} \geq \sum_{n\neq k} \frac{a_n^2 \, (W'_k - W_k)^2}{a^2_{\chi,k}} \qquad (6)$$

Since

$$\sum_{n\neq k} a_n^2 \, (W'_k - W_k)^2 = (W'_k - W_k)^2 \sum_{n\neq k} a_n^2$$

and

$$\sum_{n\neq k} a_n^2 = a^2_{\chi,k} \quad \text{by equation (1)}$$

equation (6) simplifies to

$$\tilde{\Delta}_{\chi,k} \geq (W'_k - W_k)^2 \qquad (7)$$

Finally equations (4) and (7) lead then to the upper bound under discussion:

$$a_{\chi,k} = \frac{\tilde{\Delta}_k}{\tilde{\Delta}_{\chi,k}} \leq \frac{\tilde{\Delta}_k}{(W'_k - W_k)^2} \qquad (8)$$

It will now be shown that the weak step in the derivation is the choice of W'_k which was made by Choi et al to introduce the inequality (5). Figure 1, drawn to illustrate this contention, qualitatively represents the spacings of energy levels typical for an atomic spectrum. The lengths of the vertical arrows represent $|W_m - W_k|$. In inequality (5), the basis of the derivation of the upper bound, the left hand side summation can conveniently be visualized as the sum of the weighted squared arrows. If now all arrows are replaced by the shortest one among them (arrow c), the same summation must yield a lower value: the right hand side summation in inequality (7). But if instead of arrow (c), arrow (d) were to replace all other arrows, then only arrows (c) and (b) would be replaced by a longer one. Whether then the sum will increase or decrease will entirely depend on the weighting of the arrow lengths, that is on the distribution of the a_n's. If the sum would still decrease, then a much better bound would be:

$$\frac{\tilde{\Delta}_k}{(W_{k+2} - W_k)^2}$$

This consideration leads to the following generalization.

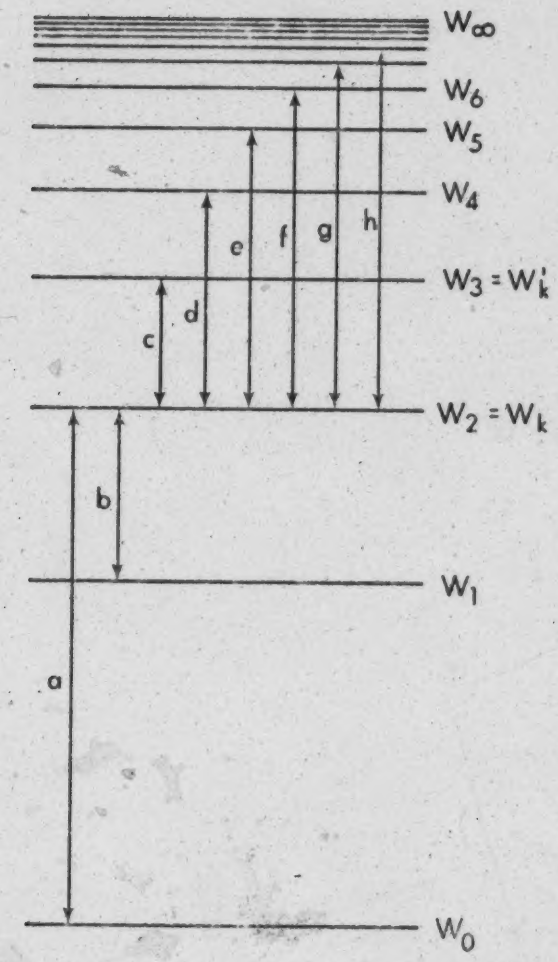

Figure 1. Hypothetical energy spectrum

The inequality: $a^2_{\chi,k} \geq \frac{\tilde{\Delta}_k}{(W_{k+m} - W_k)^2}$ may hold in which $m \geq 1$; the (unknown) distribution of the coefficients in $\Phi_k = \sum_n a_n \Psi_n$ determines the maximum value for m corresponding to the lowest, that is, best upper bound for $a^2_{\chi,k}$. It follows that the higher the maximal m, the weaker the upper bound $\tilde{\Delta}_k/(W'_k - W_k)^2$.

One can go further: a variational method may characteristically yield a distribution of a_n's which seriously weakens the bound $\tilde{\Delta}_k/(W'_k - W_k)^2$.

But even if the maximum m could be chosen, the best upper bound to $a^2_{\chi,k}$ thus obtained is not necessarily close enough to $a^2_{\chi,k}$ to be useful. This became strikingly clear when to further investigate the relation between the distribution of a_n's and the upper bound some hypothetical trial functions of ^1S states of Helium were studied.

These functions were set up as linear combinations of the ten lowest ^1S states of helium since for these the exact energy values are known (Table 14). Figure 2(a) shows the trial functions $\Phi_2(A)$ and $\Phi_2(B)$. The choice of the expansion coefficients a_0, a_1 ... a_9 was based on the reasonable assumption that a trial function Φ_k obtained by a linear variational method, if close to Ψ_k, will contain progressively less of Ψ_n as $|k - n|$

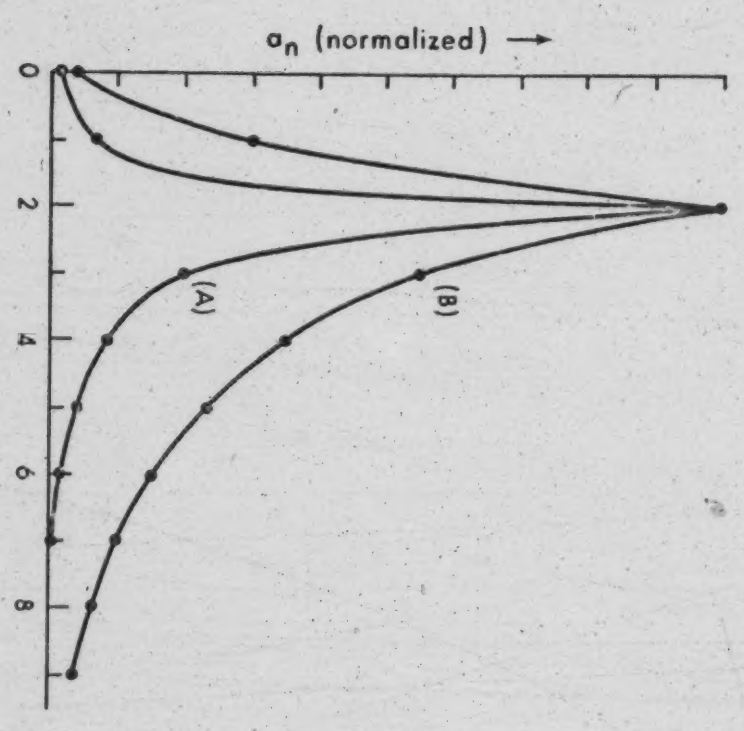

Figure 2(a). Trial functions ϕ_2.

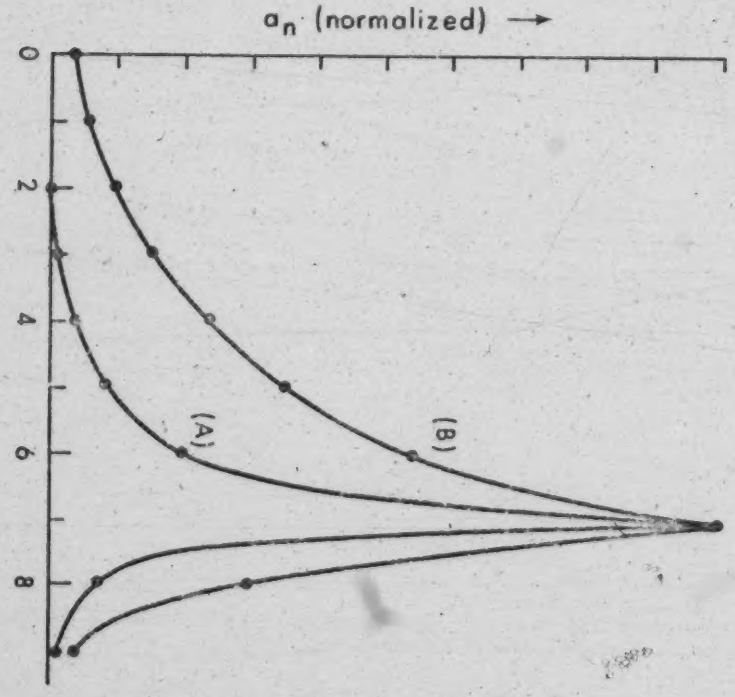

Figure 2(b). Trial functions ϕ_7.

increases. Apart from this rationale the rate of decrease of the a_n's away from a_k was arbitrarily chosen. Figure 2(b) is the mirror image of Figure 2(a) and represents trial functions $\phi_7(A)$ and $\phi_7(B)$ for the 7th excited ^1S state of helium. For the latter state two more functions were chosen, viz. $\phi_7(C)$ and $\phi_7(D)$ listed in Table 3, characterized by having small and equal expansion coefficients a_6 and a_8 corresponding to Ψ_6 and Ψ_8 respectively.

These choices along with the known W_k values (12) of the ^1S states of helium contain all information required to calculate a^2_χ and its upper bound in

$$a^2_{\chi,k} \leq \frac{\tilde{\Delta}_k}{(W'_k - W_k)^2}$$

since $a^2_{\chi,k}$ and $\tilde{\Delta}_k$ are expressed in terms of expansion coefficients and exact energies by equation (1) and (2) respectively. The results of the calculations and further comparisons are shown in Tables 1 to 4. In Table 4 the values for $a^2_{\chi,k}$ and upper bounds for all functions are listed. It is noted that all upper bounds are too high to be of any practical use except for the functions $\phi_7(C)$ and $\phi_7(D)$ which are however idealized because of their one-sided type of deviation from the exact wave-function Ψ_7.

Table 1. Trial Functions $\Phi_2(A)$ and $\Phi_2(B)$

n	$\Phi_2(A)$		$\Phi_2(B)$	
	a_n	$\tilde{\Delta}_2/(W_n - W_2)^2$	a_n	$\tilde{\Delta}_2/(W_n - W_2)^2$
0	0.0316	0.0021	0.0200	0.0005
1	0.2361	0.2118	0.0686	0.0483
2	0.7866	--	0.9742	--
3	0.4327	1.9745	0.1949	0.4520
4	0.2753	0.9414	0.0781	0.2155
5	0.1967	0.6936	0.0387	0.1588
6	0.1179	0.5900	0.0200	0.1351
7	0.0787	0.5351	0.0100	0.1225
8	0.0469	0.5021	0.0000	0.1149
9	0.0245	0.4804	0.0000	0.1100

$a^2_{\chi,2} = 0.381$ $\qquad$ $a^2_{\chi,2} = 0.051$

Table 2. Trial Functions $\Phi_7(A)$ and $\Phi_7(B)$

n	$\Phi_7(A)$		$\Phi_7(B)$	
	a_n	$\tilde{\Delta}_7/(W_n - W_7)^2$	a_n	$\tilde{\Delta}_7/(W_n - W_7)^2$
0	0.0245	0.0007	0.0000	0.0000
1	0.0469	0.0295	0.0000	0.0001
2	0.0787	0.1982	0.0100	0.0004
3	0.1179	0.8637	0.0200	0.0019
4	0.1967	3.2756	0.0387	0.0073
5	0.2753	13.3952	0.0781	0.0299
6	0.4327	87.4555	0.1949	0.1950
7	0.7866	--	0.9742	--
8	0.2361	189.3885	0.0686	0.4223
9	0.0316	64.5098	0.0200	0.1438

$a^2_{\chi,7} = 0.381$ $\qquad$ $a^2_{\chi,7} = 0.051$

Table 3. Trial Functions $\Phi_7(C)$ and $\Phi_7(D)$

n	$\Phi_7(C)$		$\Phi_7(D)$	
	a_n	$\tilde{\Delta}_7/(W_n - W_7)^2$	a_n	$\tilde{\Delta}_7/(W_n - W_7)^2$
6	0.1581	0.0359	0.0100	0.146
7	0.9747	--	0.9899	--
8	0.1581	0.0777	0.0100	0.0316
9	0.00	0.0265	0.0000	0.0108

$a^2_{\chi,7} = 0.050$ $\qquad$ $a^2_{\chi,7} = 0.020$

Table 4. Upper Bounds to $a^2_{\chi,k}$

	k	a_k	$a^2_{\chi,k}$	$\tilde{\Delta}_k/(W'_k - W_k)^2$	n	$\tilde{\Delta}_k/(W_n - W_k)^2$
ϕ_2(A)	2	0.79	0.381	1.974	9	0.480
ϕ_2(B)	2	0.97	0.051	0.452	9	0.110
ϕ_7(A)	7	0.79	0.381	189.4	3	0.864
ϕ_7(B)	7	0.97	0.051	0.422	9	0.144
ϕ_7(C)	7	0.97	0.050	0.078	8	0.078
ϕ_7(D)	7	0.99	0.020	0.032	8	0.032

We now return to the statement made earlier that it is the very choice of W_k' in $\tilde{\Delta}_k/(W_k' - W_k)^2$ which makes for a weak bound. This is now supported by the calculations of $\tilde{\Delta}_k/(W_n - W_k)^2$ for all values of n shown in the last columns of Tables 1 to 3. From each of these columns one can select the value of $\tilde{\Delta}_k/(W_n - W_k)^2$ which comes closest above the value of $a^2_{\chi,k}$. Thus one obtains the best possible upper bound by replacing W_k' with W_n in which $n \geq k' = k + 1$. These improved upper bounds are shown in the last column of Table 4.

The differences between k and n in Table 4 demonstrate clearly how far $\tilde{\Delta}_k/(W_{k+1} - W_k)^2$ is away from being a good bound. But even if in $\tilde{\Delta}_k/(W_n - W_k)^2$ the maximum n is taken to give the best upper bound to $a^2_{\chi,k}$ that bound may still be useless. This is for example illustrated with the results for $\Phi_7(A)$ in Table 4. In this case the optimization of n (n = 3) leaves the best upper bound of 0.864 still too far above the value of $a^2_{\chi,k} = 0.381$. The reason becomes clear by inspecting the column of Table 2, function $\Phi_7(A)$, from which the best upper bound was chosen. As can be seen there the reason lies in the magnitude of the intervals enclosed by the values of $\tilde{\Delta}_k/(W_n - W_k)^2$. These intervals in turn are determined by the spacings of the exact energy values. It may therefore even in principle not

be possible to obtain a useful upper bound to the squared deviation coefficient $a^2_{\chi,k}$, even if in some way the best bound expressed as $a^2_{\chi,k} \leq \tilde{\Delta}_k/(W_n - W_k)^2$ could be found.

The conclusion must therefore be that the functional $\tilde{\Delta}_k/(W'_k - W_k)^2$ is not a useful upper bound to $a^2_{\chi,k}$; or, in other words, the minimization of $\tilde{\Delta}_k$ does not provide a useful lower bound to the overlap a_k. Supporting numerical evidence will be presented in Chapter III.

That $\tilde{\Delta}_k$ and $\varepsilon_k^2/\tilde{\Delta}_k$ are not good measures of a_k does, however, not invalidate Messmer's proposal to maximize a_k by minimizing the functionals simultaneously. The problem to be investigated is to find the proper minimization procedure. To that end a comparative study was undertaken of ε_k and $\tilde{\Delta}_k$ minimization by a combination of linear and non-linear variation, as described in detail in Chapter II.

The results, reported in Chapter III, show that the simultaneous minimization of $\varepsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$ was, at least in the cases considered, best achieved by the ε_k minimization. In fact it was this finding which induced the author to discontinue computation or minimization of $\tilde{\Delta}_k$ in favor of searching for excited state wave functions by the Rayleigh-Ritz variational method mentioned earlier.

II. Computational Procedures

The Hamiltonian used here is the non-relativistic, spin-independent, infinite-nuclear-mass Schroedinger Hamiltonian for two electrons:

$$H = H_1 + H_2 + \frac{1}{r_{12}} \tag{1}$$

in which

$$H_i = \frac{-\nabla_i^2}{2} - \frac{Z}{r_i} ,$$

the one-electron operator for electron i.

The squared Hamiltonian H^2 used in the calculation of $\tilde{\Delta}_k$ is obtained by expansion:

$$H^2 = (H_1 + H_2 + \frac{1}{r_{12}})(H_1 + H_2 + \frac{1}{r_{12}})$$

$$= H_1^2 + H_2^2 + 2H_1H_2 + (H_1 \frac{1}{r_{12}} + \frac{1}{r_{12}} H_1)$$

$$+ (H_2 \frac{1}{r_{12}} + \frac{1}{r_{12}} H_2) + (\frac{1}{r_{12}})^2 \tag{2}$$

The trial function Φ_k, being an approximation to the exact state function Ψ_k, is a configuration interaction (CI) function of the form:

$$\Phi_k = \sum_{i=1}^{N} v_{ik} \phi_i \tag{3}$$

The basis $\phi_1, \phi_2, \ldots \phi_N$ is a set of ^1S two-electron configuration functions. Thus if in ϕ_i an orbital function for electron k is denoted by $(n_k,\ell,m)_i$ and if 1 and 2 refer to electron 1 and electron 2 we have (20):

$$\phi_i \equiv \phi_i(1,2) \equiv [\Phi_i(1,2)]\ ^1S$$

$$= \sum_{m=-\ell}^{\ell} \frac{(-1)^{\ell+m}}{\sqrt{2\ell+1}} \frac{1}{\sqrt{2}} [(n_1,\ell,m)_i(n_2,\ell,-m)_i + (n_2,\ell,-m)_i(n_1,\ell,m)_i]$$

$$\times \frac{1}{\sqrt{2}} [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \qquad (4)$$

with α and β spin functions of an electron.

In the case of double occupancy in ϕ_i duplication of terms occurs in the above summation. This follows from the symmetry of the above expansion if $n_1 = n_2$ while m runs from $-\ell$ to $+\ell$. With $n_1 = n_2 = n$, equation (4) simplifies to:

$$\phi_i(1,2) = \sum_{m=-\ell}^{\ell} \frac{(-1)^{\ell+m}}{\sqrt{2\ell+1}} \frac{2}{\sqrt{2}} [(n,\ell,m)_i(n,\ell,-m)_i]$$

$$\times \frac{1}{\sqrt{2}} [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \qquad (5)$$

The CI basis is determined by two choices: first the choice of the configurations, i.e., the choice of n_1, n_2 and ℓ in equation (4) or (5) for each ϕ_i, and

secondly, the choice of the basis functions, that is the one-electron or orbital functions for (n_k, ℓ, m) in equation (4) or (5).

One choice has been the complete, orthonormal set of associated Laguerre orbital functions:

$$(n_i, \ell, m) = N_c (2\eta r)^{\ell} e^{-\eta r} L^{2\ell+1}_{n_i+\ell+1}(2\eta r)\, P_{\ell}^{|m|}(\cos\theta)\, e^{im\phi} \qquad (6)$$

in which N_c is a normalization factor; η, the orbital exponent, functions as a non-linear variational parameter If in the CI basis all Laguerre orbitals have the same value assigned to η, the basis itself is, of course, also orthonormal.

Non-orthogonal CI bases were also used by expressing $[\phi_i(1,2)]^1S$ in Slater type orbitals (STO's). In that case

$$(n_i, \ell, m) = r^{n_i-1}\, e^{-\eta r}\, P_{\ell}^{|m|}(\cos\theta)\, e^{im\phi} \qquad (7)$$

The minimizations of ε_k and $\tilde{\Lambda}$ by linear variation were carried out by solving a matrix eigen value problem of the general form:

$$\underset{\sim}{M}\,\underset{\sim}{V} = \underset{\sim}{S}\,\underset{\sim}{V}\,\underset{\sim}{\lambda} \qquad (8)$$

on the CI basis $\phi_1, \phi_2, \ldots \phi_N$.

For ε_k minimization, which entails E_k minimization since $\varepsilon_k = |E_k - W_k|$,

$$\underset{\sim}{M}_{ij} = \langle \Phi_i | H | \Phi_j \rangle \tag{9}$$

and for $\tilde{\Delta}_k$ minimization

$$\underset{\sim}{M}_{ij} = \langle \Phi_i | (H - W_k)^2 | \Phi_j \rangle \tag{10}$$

$\underset{\sim}{S}$ is the metric matrix with

$$\underset{\sim}{S}_{ij} = \langle \Phi_i | \Phi_j \rangle \tag{11}$$

If the basis is orthonormal, $\underset{\sim}{S}$ is the identity matrix $\underset{\sim}{I}$ and matrix equation (8) simplifies to:

$$\underset{\sim}{M}\ \underset{\sim}{V} = \underset{\sim}{V}\ \underset{\sim}{\lambda} \tag{12}$$

If the basis was non-orthogonal, equation (8) was reduced to the form of equation (12) by a canonical orthogonalization transformation (21). This transformation entails a method to construct a matrix $\underset{\sim}{T}$ such that

$$\underset{\sim}{T}^t\ \underset{\sim}{S}\ \underset{\sim}{T} = \underset{\sim}{I} \tag{13}$$

Using the fact that $\underset{\sim}{T}\underset{\sim}{T}^{-1} = I$ equation (8) can be rewritten as:

$$\underset{\sim}{T}^t\ \underset{\sim}{M}\ \underset{\sim}{T}\ \underset{\sim}{T}^{-1}\ \underset{\sim}{V} = \underset{\sim}{T}^t\ \underset{\sim}{S}\ \underset{\sim}{T}\ \underset{\sim}{T}^{-1}\ \underset{\sim}{V}\ \underset{\sim}{\lambda} \tag{14}$$

and by introducing

$$\underset{\sim}{M'} = \underset{\sim}{T}^{t}\ \underset{\sim}{M}\ \underset{\sim}{T} \tag{15}$$

and

$$\underset{\sim}{V'} = \underset{\sim}{T}^{-1}\ \underset{\sim}{V} \tag{16}$$

equation (14) simplifies to:

$$\underset{\sim}{M'}\ \underset{\sim}{V'} = \underset{\sim}{V'}\ \underset{\sim}{\lambda} \tag{17}$$

The equations (12) and (17) permit solution by diagonalizing $\underset{\sim}{M}$ and $\underset{\sim}{M'}$, which yields the matrix $\underset{\sim}{V}$ and $\underset{\sim}{V'}$ of the eigen vectors and the diagonal matrix $\underset{\sim}{\lambda}$ of the eigen values. All diagonalizations were carried out by the classic Jacobi method (22).

For E_k minimization the diagonalization can be written as:

$$\underset{\sim}{C}^{-1}\ \underset{\sim}{H}\ \underset{\sim}{C} = \underset{\sim}{E} \tag{18}$$

in which $\underset{\sim}{H}$ is the matrix representation of H according to equation (9), transformed to an orthogonal basis if necessary. The results of interests are here the columns $\vec{C}_k$ of $\underset{\sim}{C}$ as vector representations of the CI function Φ_k and the corresponding E_k values, the diagonal elements of $\underset{\sim}{E}$, which serve as minimized upper bounds to the true state energies W_k. According to equation (18) the CI

function Φ_k belonging to E_k is then:

$$\Phi_k = \sum_{i=1}^{N} c_{ik} \phi_i \qquad (19)$$

In the $\tilde{\Delta}_k$ minimization the subscript k plays, it should be pointed out, a different role since now k labels the operator $(H - W_k)^2$ rather than the eigen values and vectors as above. Let $\underset{\sim}{D}_k$ be the matrix representation of $(H - W_k)^2$ according to equation (10), transformed to an orthogonal basis if required. The diagonalization can then be presented as:

$$\underset{\sim}{L}^{-1} \underset{\sim}{D}_k \underset{\sim}{L} = \tilde{\Delta}_k \qquad (20)$$

A set of eigen values $\{(\tilde{\Delta}_k)_i\}$ is obtained of which now only the lowest, hereafter denoted by $\tilde{\Delta}_k$, is of interest. The corresponding eigen vector will be called $\vec{L}^{(k)}$ and the CI function belonging to $\tilde{\Delta}_k$ is then:

$$\Phi_k = \sum_{i=1}^{N} \ell_i^{(k)} \phi_i \qquad (21)$$

If E_k is obtained by diagonalization according to equation (18) the quantity $\tilde{\Delta}_k$ can be calculated from the Φ_k obtained. By the definition of $\tilde{\Delta}_k$ as

$$\tilde{\Delta}_k = \langle \Phi_k | (H - W_k)^2 | \Phi_k \rangle$$

and with Φ_k as in equation (19), $\tilde{\Delta}_k$ is calculated by:

$$\tilde{\Delta}_k = \sum_{i,j}^{N} c_{ik} (D_k)_{ij} c_{jk} \qquad (22)$$

If, on the other hand, $\tilde{\Delta}_k$ is obtained by diagonalization according to equation (20), E_k can be calculated from the Φ_k obtained. From the definition of E_k as

$$E_k = \langle \Phi_k | H | \Phi_k \rangle$$

with Φ_k as in equation (21), E_k is calculated by:

$$E_k = \sum_{i,j=1} \ell_i^{(k)} \tilde{H}_{ij} \ell_j^{(k)} \qquad 23)$$

Separate computer programs were developed for the minimization work with the Laguerre and Slater type orbitals. The correctness of both programs was confirmed by complete duplication of published Helium ground states on bases of twenty configurations, respectively by Holoien (9) and Weiss (10). All computations were carried out in double precision on the IBM 360/67 computer of the University of Alberta Computing Centre.

III. The Simultaneous Minimization of $\epsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$

III.1 Introduction

Choi et al (7) originally proposed the simultaneous minimization of $\epsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$ in the context of self-consistent-field theory for excited states because then ϵ_k alone is not an adequate criterion for obtaining a good wave function. In the present work with configuration interaction, the MacDonald theorem does permit the use of ϵ_k as criterion since there exist well-defined lower bounds to each approximate state energy. It then becomes of interest to enquire whether there are large discrepancies in the nature of the minimization process using the $\epsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$ versus ϵ_k minimization methods.

III.2 Separate Minimization of ϵ_k and $\tilde{\Delta}_k$

Separate minimizations of ϵ_o and $\tilde{\Delta}_o$ were applied to the ground states of He, Li^+ and Be^{++}. For comparison these were all carried out on the same configuration basis. This basis, a set of ten configurations, is basis VI listed in Table 10 and is expressed in the associated Laguerre functions described in Chapter II.*

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* Further details of the basis are given in Chapter IV.

The results are listed in Tables 5 and 6 and plotted in Figures 3, 4, and 5. In Figures 3(a), 4(a), and 5(a) each plotted point on the curves labelled ε_o represents the minimized ε_o obtained by linear variation at the indicated value of η. To each ε_o value belongs a trial function Φ_o. From this Φ_o, $\tilde{\Delta}_o$ and $\varepsilon_o^2/\tilde{\Delta}_o$ are calculated by:

$$\tilde{\Delta}_o = \langle \Phi_o | (H - W_o)^2 | \Phi_o \rangle$$

and

$$\varepsilon_o^2/\tilde{\Delta}_o = (E_o - W_o)^2/\tilde{\Delta}_o .$$

Thus the ε_o minimization produces three curves for a ground state: the ε_o-curve obtained by variation and the $\tilde{\Delta}$- and $\varepsilon^2/\tilde{\Delta}$-curves calculated from the trial functions corresponding to the ε_o-curve. Similarly, as shown in Figures 3(b), 4(b), and 5(b), the $\tilde{\Delta}_o$ minimization leads to three curves: the $\tilde{\Delta}$ curve by variation, the ε_o-curve and $\varepsilon^2/\tilde{\Delta}$-curve by calculation from the trial functions corresponding to the $\tilde{\Delta}$-curve. For comparison all minima are given in Table 7.

The following observations are made:

i) In the ε_o minimizations [Figures 3(a), 4(a), and 5(a), and Table 7] ε_o and $\tilde{\Delta}_o$ obtain lowest values practically simultaneously, i.e., at nearly the same value of η.

For He the lowest ε_o and $\tilde{\Delta}_o$ coincide at $\eta = 2.325$; for Li^+ and Be^{++} the differences between the η values at which ε_o and $\tilde{\Delta}_o$ are lowest are respectively 0.05 and 0.1.

ii) In the $\tilde{\Delta}_o$ minimization [Figures 3(b), 4(b), and 5(b), and Table 7] $\tilde{\Delta}_o$ and ε_o reach lowest values simultaneously only in the case of Be^{++} at $\eta = 5.15$. For He and Li^+, ε_o and $\tilde{\Delta}_o$ reach minima at η values which differ respectively by 0.3 and 0.15.

iii) In all cases the lowest value of $\varepsilon_o^2/\tilde{\Delta}_o$ coincides with that of ε_o with respect to η, whether ε_o is obtained directly by ε_o or indirectly by $\tilde{\Delta}_o$ minimization. (Figures 3, 4, and 5, and Table 7).

iv) For each ground state the ε_o minimization yields values of ε_o and $\varepsilon_o^2/\tilde{\Delta}_o$ much lower than the $\tilde{\Delta}_o$ minimization (Table 7).

These observations clearly show that in these applications of the Rayleigh-Ritz method the ε_k minimizations come very close to satisfying the criterion of simultaneous decrease of $\varepsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$.

A further example is presented in Table 8. This is a comparison of four trial functions for the ground state of He, all obtained by ε_o minimization, each on a different configuration basis. From each trial function

Table 5. E_o minimization

	η	ε_o (a.u.)	$\tilde{\Delta}_o$	$(\varepsilon_o^2/\tilde{\Delta}_o)$ x 10^4
	2.250	0.0035902	0.22865	0.5637
	2.300	0.0035106	0.22734	0.5421
He	2.325	0.0034999	0.22721	0.5391
	2.350	0.0035099	0.22746	0.5416
	2.400	0.0035964	0.22931	0.5640
	2.450	0.0037804	0.23327	0.6127
	3.40	0.0050481	0.6872	0.3746
	3.50	0.0047908	0.6740	0.3301
	3.60	0.0044646	0.6661	0.3027
Li^+	3.65	0.0044096	0.6649	0.2959
	3.70	0.0043995	0.6660	0.2940
	3.75	0.0044398	0.6698	0.2977
	3.85	0.0046972	0.6878	0.3243
	4.00	0.0056415	0.7504	0.4280
	4.00	0.009628	1.5809	0.5865
	4.50	0.006849	1.4164	0.3311
	4.75	0.005973	1.3597	0.2624
Be^{++}	4.90	0.005675	1.3428	0.2399
	5.00	0.005608	1.3438	0.2340
	5.10	0.005678	1.3594	0.2371
	5.25	0.006111	1.4207	0.2629
	5.50	0.010077	1.6801	0.3883

Note: The above data are plotted in Figures 3(a), 4(a), and 5(a).

Table 6. $\tilde{\Delta}_o$ minimization

	η	$\tilde{\Delta}_o$	ε_o(a.u.)	$(\varepsilon_o^2/\tilde{\Delta}_o)$ x 10^4
	2.10	0.1951	0.0226	26.370
	2.20	0.1930	0.0180	16.940
	2.30	0.1924	0.0143	10.714
He	2.40	0.1936	0.0115	6.929
	2.50	0.1969	0.0098	4.960
	2.60	0.2027	0.0092	4.237
	2.70	0.2115	0.0102	4.918
	2.80	0.2240	0.0128	7.331
	3.50	0.6175	0.0123	2.505
	3.65	0.6084	0.0102	1.711
	3.75	0.6055	0.0091	1.379
	3.80	0.6056	0.0087	1.264
Li^+	3.85	0.6062	0.0085	1.202
	3.90	0.6080	0.0084	1.159
	3.95	0.6108	0.0085	1.171
	4.00	0.6149	0.0087	1.242
	4.10	0.6270	0.0100	1.557
	4.80	1.2746	0.01038	0.8441
	4.90	1.2624	0.00959	0.7278
	5.00	1.2533	0.00896	0.6407
Be^{++}	5.10	1.2480	0.00857	0.5886
	5.15	1.2471	0.00849	0.5779
	5.20	1.2474	0.00850	0.5790
	5.30	1.2523	0.00885	0.6246
	5.40	1.2638	0.00972	0.7473

Note: the above data are plotted in Figures 3(b), 4(b), and 5(b).

Table 7. Minima of ε_o, $\tilde{\Delta}_o$ and $\varepsilon_o^2/\tilde{\Delta}_o$

	η	ε_o (a.u.)	η	$\tilde{\Delta}_o$	η	$(\varepsilon_o^2/\tilde{\Delta}_o) \times 10^4$
He:						
by E_o minimization	2.325	0.003499	2.325	0.2272	2.325	0.5391
by $\tilde{\Delta}_o$ minimization	2.60	0.0092	2.30	0.1924	2.60	4.237
Li^+:						
by E_o minimization	3.70	0.0043995	3.65	0.6649	3.70	0.2940
by $\tilde{\Delta}_o$ minimization	3.90	0.0084	3.75	0.6055	3.90	1.159
Be^{++}:						
by E_o minimization	5.00	0.005608	4.90	1.3428	5.00	0.2340
by $\tilde{\Delta}_o$ minimization	5.15	0.00849	5.15	1.2471	5.15	0.5779

Note: the minima are obtained from Tables 5 and 6.

Table 8. ε_o minimizations with different bases; Helium

Basis	η	ε_o (a.u.)	$\tilde{\Delta}_o$	$(\varepsilon_o^2/\tilde{\Delta}_o)$ x 10^{-4}
No. I in Table 10	2.005	0.02513	0.4282	14.74
No. VI. in Table 10	2.325	0.00350	0.2272	0.54
No. III in Table 10	2.222	0.00249	0.1932	0.32
Weiss (10)	--	0.00103	0.1427	0.07

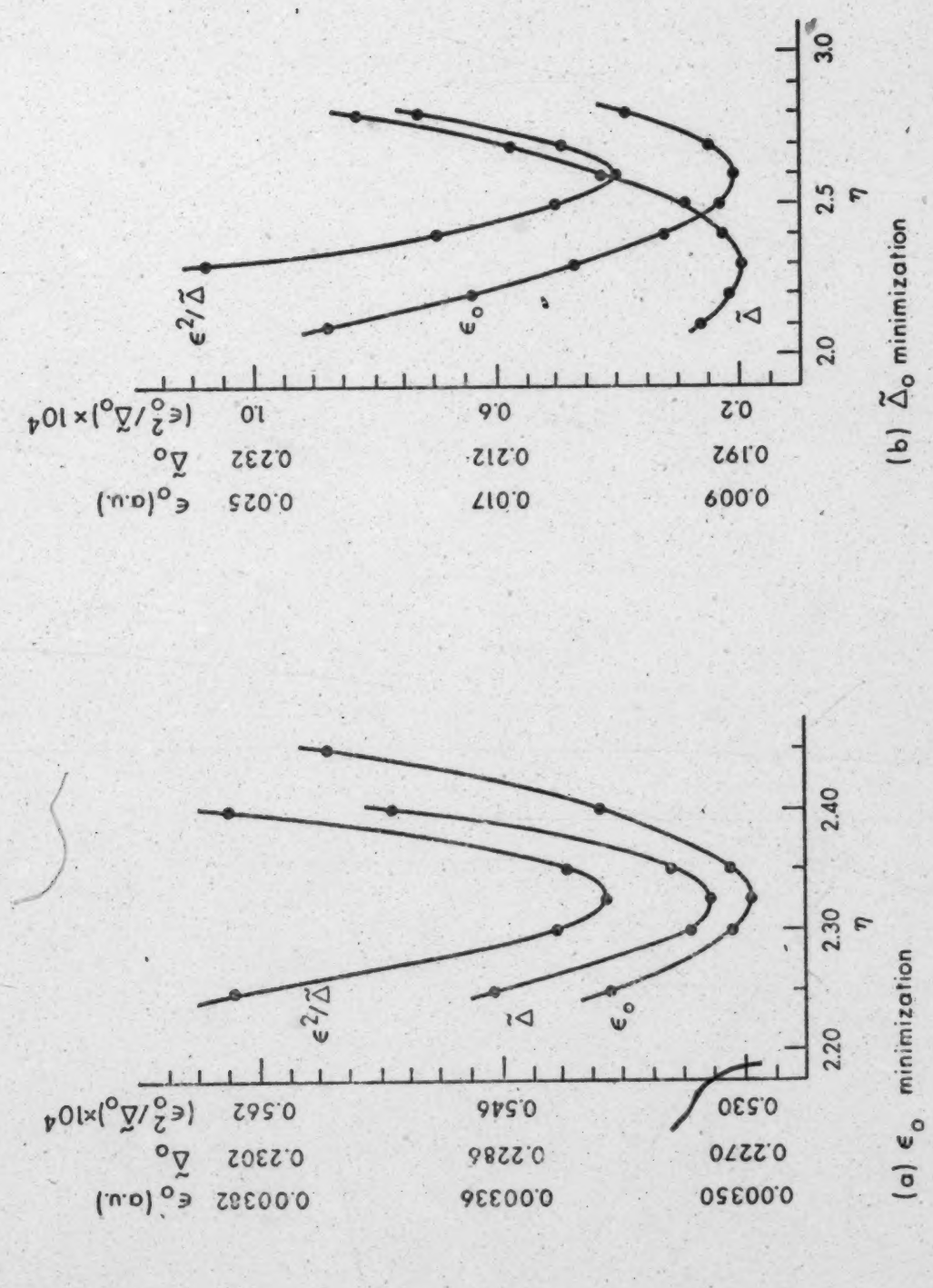

Figure 3. Ground state of He.

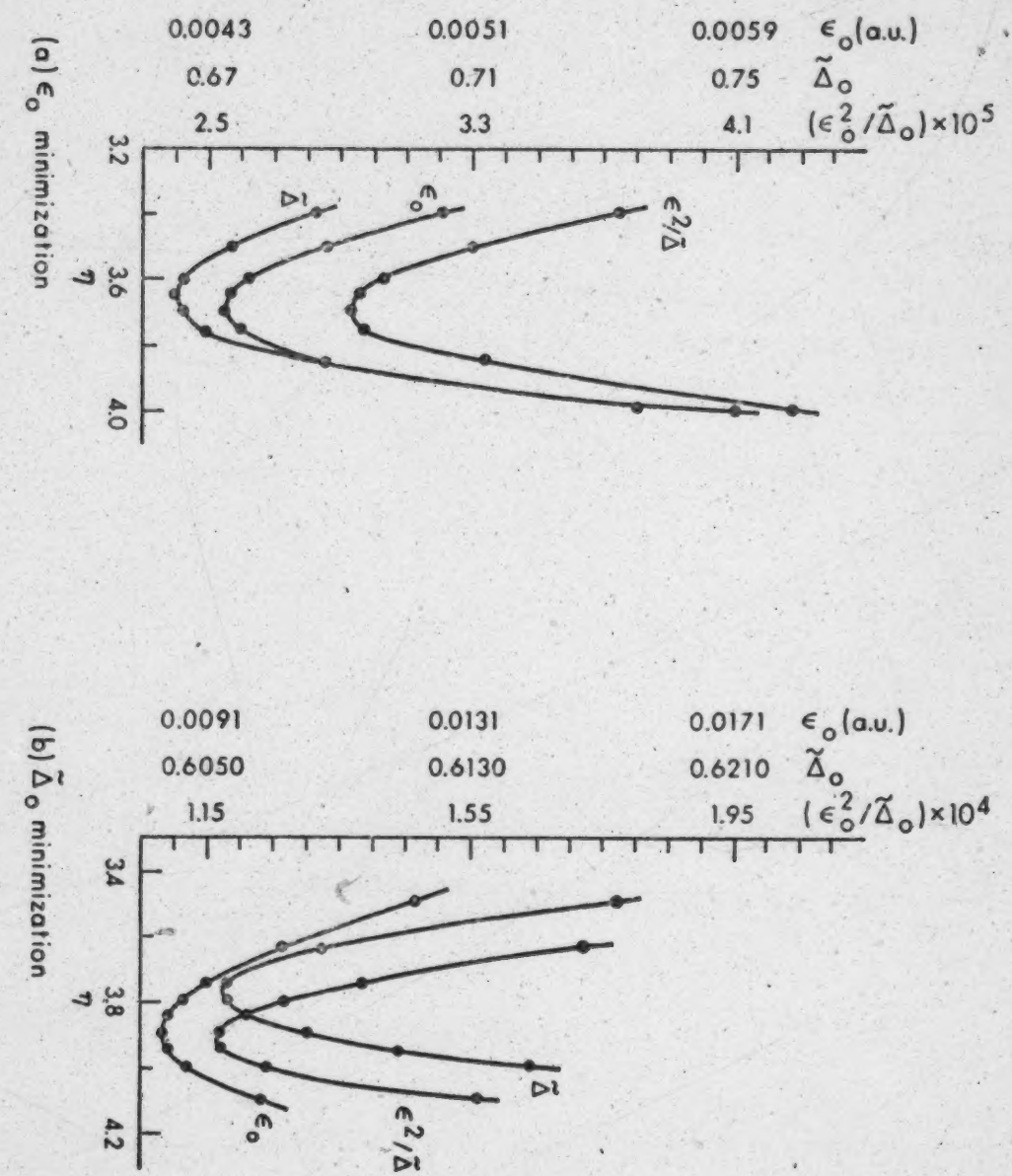

Figure 4. Ground state of Li^+

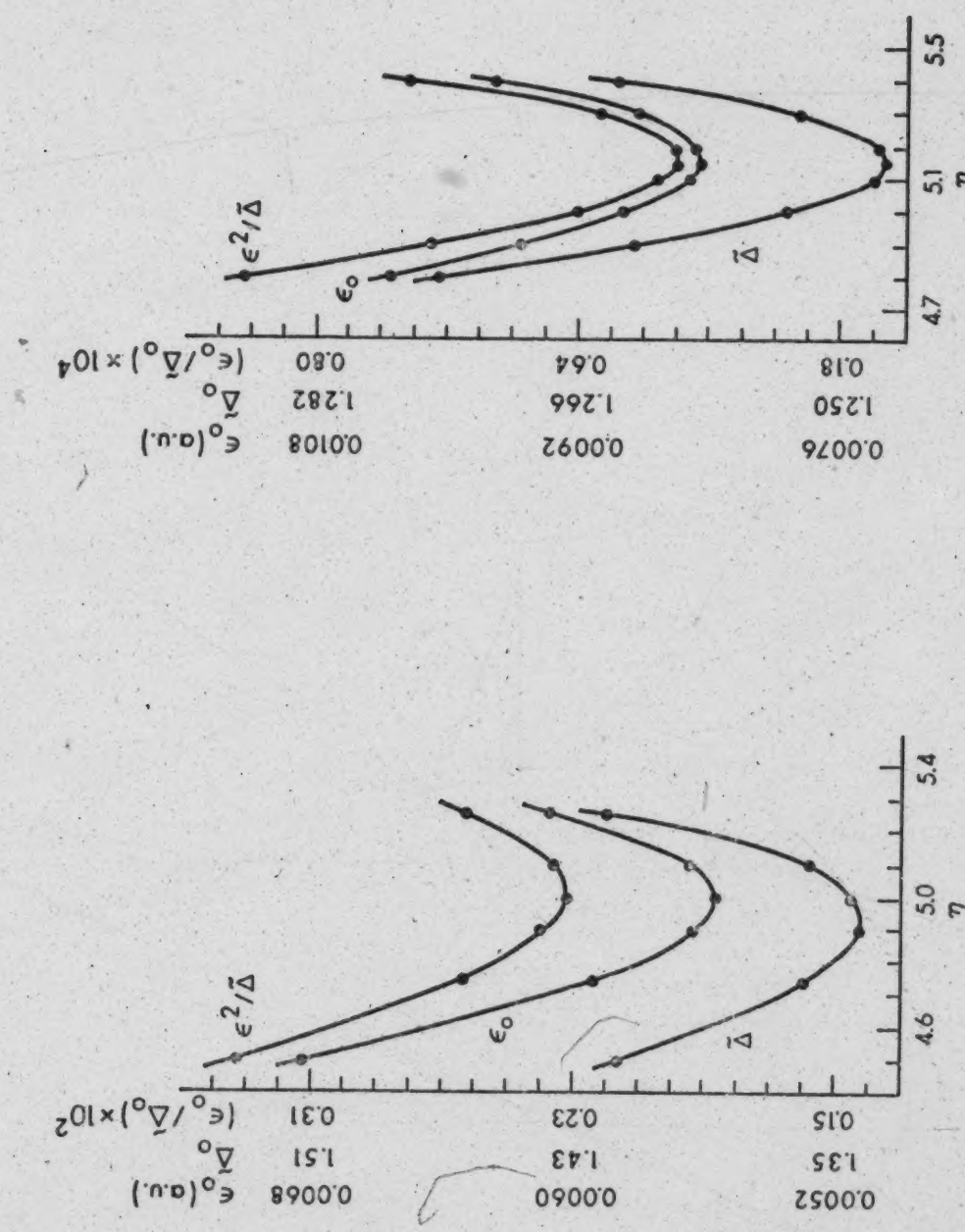

Figure 5. Ground state of Be^{++}.

$\tilde{\Delta}_o$ and $\varepsilon_o^2/\tilde{\Delta}_o$ were calculated. It is seen in the table that the lower the value of ε_o the lower are the values of $\tilde{\Delta}_o$ and $\varepsilon_o^2/\tilde{\Delta}_o$. As in the preceding case the criteria of lowest ε_k and lowest $\varepsilon_k^2/\tilde{\Delta}_k$ run parallel. By either criterion the four trial functions would be arranged in the same order of goodness.

III.3 Conclusions

The above analysis leads to the following decisions. First, the minimization of $\tilde{\Delta}_k$ alone is rejected in favour of ε_k minimization. The reasons are that the simultaneous decrease of ε_k and $\tilde{\Delta}_k$ is best approached in the ε_k minimization [observations (i) and (ii) above] and that the lowest values for ε_k^2 and $\varepsilon_k^2/\tilde{\Delta}_k$ are obtained by ε_k minimization [observation (iv) above].

Secondly, in the ε_k minimization the calculations of $\tilde{\Delta}_k$ and $\varepsilon_k^2/\tilde{\Delta}_k$ can be omitted since they do not significantly add to the information provided by the ε_k minimization [observation(iii) above]. This has also the great advantage of cost reduction since the calculation of $\tilde{\Delta}_k$ requires far more computer time than that of ε_k.

In conclusion: The Rayleigh-Ritz variational method is found to very closely satisfy Messmer's criterion that $\varepsilon_k^2/\tilde{\Delta}_k$ and $\tilde{\Delta}_k$ should decrease simultaneously. This

being so there appears to be no gain in using the methods involving $\tilde{\Delta}_k$ as an alternative to minimization of ε_k in context where the MacDonald theorem makes ε_k minimization a viable technique.

III.4 The Upper Bound $\tilde{\Delta}_k/(W_k' - W_k)^2$

The work on the ground states of He, Li^+, and Be^{++} reported above produced some data which are pertinent to the upper bound $\tilde{\Delta}_k/(W_k' - W_k)^2$.

It was pointed out in Chapter I that the weakness of the bound follows necessarily from the spacings in the atomic energy spectrum. This was illustrated with a hypothetical energy spectrum. Some supporting numerical results can now be presented. These are obtained from the ε_o minimizations, reported above, on the same basis for He, Li^+, and Be^{++} (Table 7). From the trial functions belonging to the ε_o's the values of $\tilde{\Delta}_o$ are calculated, and since the accurate values of $|W_1 - W_o|$ are known (17), the upper bounds $\tilde{\Delta}_o/(W_1 - W_o)^2$ can be calculated. The results are listed in Table 9.

Since $\tilde{\Delta}_k$ is defined by $\tilde{\Delta}_k = \langle \Phi_k | (H - W_k)^2 | \Phi_k \rangle$, $\tilde{\Delta}_k \to 0$ as $\Phi_k \to \Psi_k$. Bearing this in mind one would conclude from the $\tilde{\Delta}_o$ values in Table 9 that, for example, Φ_o of He with $\tilde{\Delta}_o = 0.2272$ should be a more accurate trial function than Φ_o of Be^{++} with $\tilde{\Delta}_o = 1.3438$. However, the

Table 9. Upper Bounds to $a^2_{\chi,k}$ by ε_o minimization

System	ε_o minimization		$\tilde{\Delta}_o$	$\lvert W_1 - W_o \rvert$ (17) (a.u.)	$\tilde{\Delta}_o/(W_1 - W_o)^2$
	η	ε_o(a.u.)			
He	2.325	0.0035	0.2272	0.7283	0.4283
Li^+	3.70	0.0044	0.5660	2.1690	0.1416
Be^{++}	5.00	0.0056	1.3438	4.3581	0.0708

upper bounds would lead to the opposite conclusion. These bounds, being 0.4283 for He and 0.0708 for Be^{++}, imply that the squared deviation coefficient $a^2_{\chi,k}$ of ϕ_k for He could be six times that of ϕ_k for Be^{++}.

The reason for this reversal lies in the values of $|W_1 - W_o|$ as can be seen in the table. Since Be^{++} has the largest $|W_1 - W_o|$ value and since the upper bound is inversely proportional to $(W_1 - W_o)^2$ the ϕ_k of Be^{++} would appear the poorest according to its $\tilde{\Delta}_o$ value and the best by its $\tilde{\Delta}_o/(W_1 - W_o)^2$ value.

These results therefore clearly illustrate that $\tilde{\Delta}_k/(W'_k - W_k)^2$ cannot be expected to be a dependable upper bound.

IV. The application of the Rayleigh-Ritz Variational Method

IV.1 Introduction

As discussed in the preceding chapter a comparative study of ε_k and $\bar{\Delta}_k$ minimizations decided in favor of applying the Rayleigh-Ritz variational method for the calculation of excited states. In this chapter the search for excited state wave functions based on this method will be reported. In the course of this study a number of bases were generated which, for convenient reference, are collected in Table 10. These bases represent a gradual improvement in their ability to generate trial functions with energies close to the true energies. The study culminates in finding a basis which firmly establishes the great promise of the Rayleigh-Ritz method for excited state wave functions.

Shortly after the conclusion of this work a publication by Wang and Weinhold appeared in the literature (15) dealing with excited state wave functions of helium obtained by the Rayleigh-Ritz variational method. This paper is the first to deal with the application of this approach in the literature, and therefore merits a separate discussion below. In this connection one particular basis set investigated in this work is of

Table 10. Configuration Bases

Basis No.	Number of Configurations	Configurations
I	10	$(1s)^2$, 1s2s, $(2s)^2$, 1s3s, 2s3s, $(3s)^2$, 1s4s, 2s4s, 3s4s, $(4s)^2$
II	15	I + 1s5s, 2s5s, 3s5s, 4s5s, $(5s)^2$
III	20	I + $(2p)^2$, 2p3p, $(3p)^2$, 2p4p, 3p4p, $(4p)^2$, $(3d)^2$, 3d4d, $(4d)^2$, $(4f)^2$
IV	20	II + $(2p)^2$, 2p3p, $(3p)^2$, 2p4p, 3p4p
V	15	$(1s)^2$, 1s2s, 1s3s, ..., 1s15s
VI	10	$(1s)^2$, 1s2s, 1s3s, $(2p)^2$, 1s4s, $(2s)^2$, 2s3s, $(3d)^2$, $(3p)^2$, 2s4s

special importance since it shows flaws which help to explain inaccuracies in Wang and Weinhold's excited state energies.

IV.2 The development of basis sets

The first concern in this study was to obtain some idea of the results one could get with the Rayleigh-Ritz variational method. For this purpose the choice of the bases could be arbitrary and fell on a basis which had been published by Holoien (9) as being a good one for the ground state of helium. This basis (No. II in Table 10) is expressed in the Laguerre functions described in Chapter II. With the orbital exponent optimized to 2.222 the basis generates a ground state energy of -2.90123 a.u. which compares with Pekeris' (12) highly accurate value of -2.90372 a.u.

Although this basis cannot be expected to give good approximations to the excited states in the E_k minimization to be explored, the results are still of interest for two reasons.

First, they illustrate the type of minimization curves generally obtained in this work. As shown in Figure 6 a set of E_k values is obtained by linear variation for a specific value of the orbital exponent η. Since the basis has 20 configurations, 20 upper

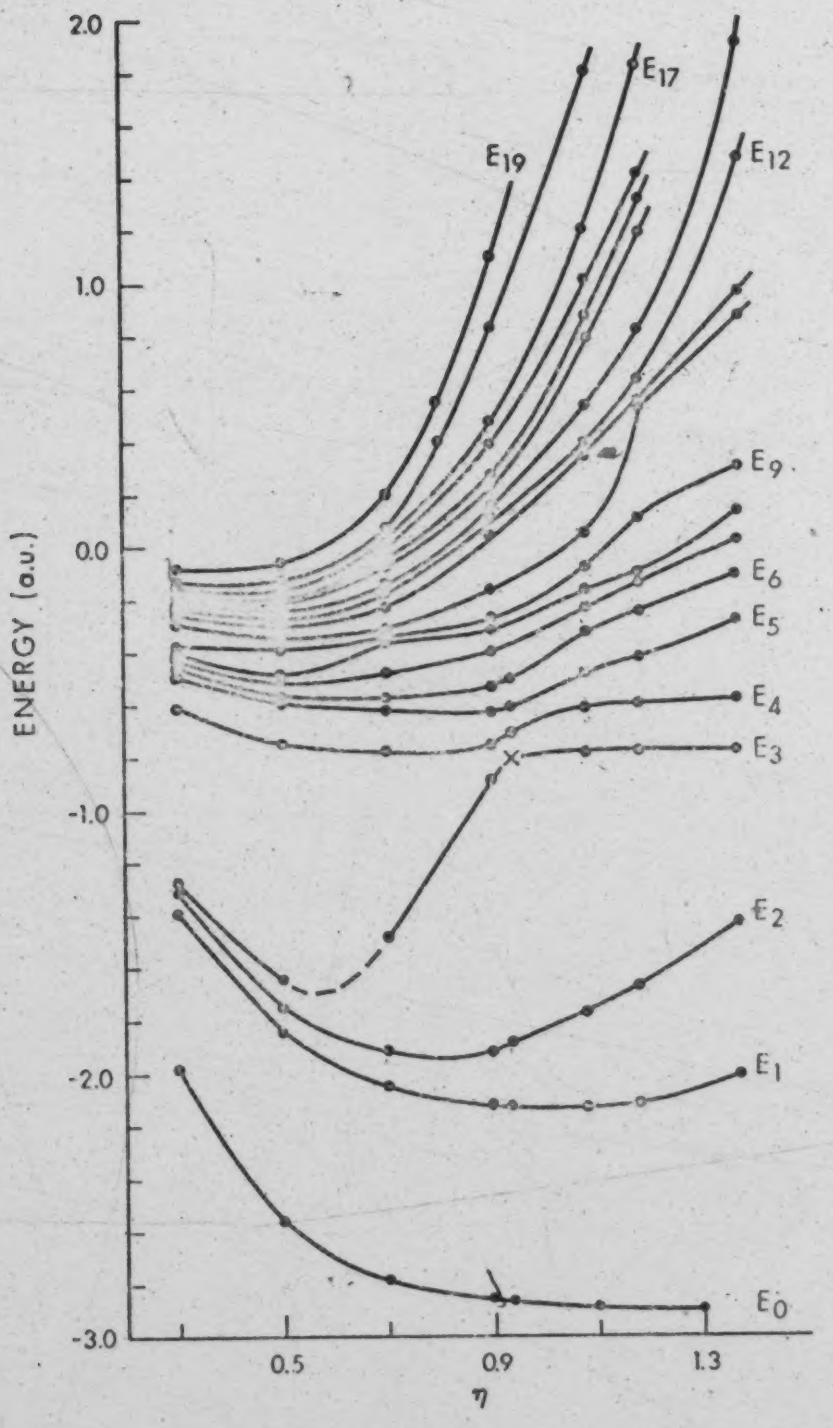

Figure 6. E_K minimization by variation of η.

bounds E_k values were obtained. The minimum for each E_k was then established by non-linear variation, i.e., the variation of η. As shown in the figure, a minimization curve is thus obtained for each E_k value. The minima of the curves are listed in Table 11 as E_k, η pairs. As to be expected the minimized E_k values are useless as upper bounds. All of them, except E_o and E_1, lie even above the series limit of -2.0 a.u. of the singly excited ^1S states of helium.

Secondly, the results illustrate a viewpoint stated earlier by the author. This was that generally in work on ground states the Rayleigh-Ritz method would yield upper bounds too high to encourage attempts to improve these for excited states. A case in point is provided by the upper bounds obtained with the minimization of E_o at $\eta = 2.222$. They are listed in the fourth column of Table 11. These E_k values are indeed too high to even remotely suggest a possible use as upper bounds. On the other hand, it is worth noting that the non-linear variation does bring about an impressive lowering of the upper bounds just mentioned (Table 11, columns 2 and 4). This is however, by itself still far from sufficient, as evident from a comparison with the exact values W_k given in the last column of the table.

Further improvement is therefore to be sought

Table 11. E_k minimization; Basis No. III.

k	E_k minimized (a.u.)	η optimal	E_k $\eta = 2.222$ (a.u.)	W_k (a.u.) (a)
19	-0.777	0.30	28.1392	
18	-0.1292	0.50	15.6082	
17	-0.1535	0.30	14.1936	
16	-0.1687	0.50	13.1639	
15	-0.1958	0.50	12.2738	
14	-0.2166	0.50	8.0727	
13	-0.2439	0.40	7.2688	
12	-0.2689	0.50	6.4925	
11	-0.3046	0.50	3.9823	-2.0035838
10	-0.3479	0.50	3.4065	--
9	-0.3911	0.30	3.3017	-2.0051690
8	-0.4925	0.50	2.2062	-2.0063690
7	-0.5064	0.50	1.4873	-2.0080917
6	-0.5788	0.70	0.9865	-2.0106203
5	-0.6177	0.90	0.9052	-2.0145597
4	-0.7732	0.70	0.3806	-2.0211723
3	-1.6377	0.80	-0.3034	-2.0335801
2	-1.9286	0.80	-0.5368	-2.0612621
1	-2.1336	1.08	-1.7978	-2.1459533
0	-2.9012	2.22	-2.9012	-2.9037244

(a) References in Table 14.

in changing the basis itself, by varying and optimizing its composition and length. To study the composition with fixed length two sets each containing 10 configurations were selected from Holoien's basis just discussed (No. III in Table 10). The one selection is basis No. I which is simply the first 10 radial terms of basis No. III. The other selection is basis No. VI. This set was selected by analysis of the trial function for the ground state obtained from basis No. III at $n = 2.222$. From this function were chosen the ten configurations with the highest expansion coefficients, that is, the ten energetically dominant configurations.

The results obtained from these sets are given in Table 12 and Figure 7. They are of interest specifically with respect to the most serious problem in CI calculations, namely the selection of those configurations which lead to a most rapid convergence toward a specific state. There is no general rule available for choosing such configurations (3). Figure 7 shows the superiority of basis No. VI over basis No. I in terms of convergence towards the true ground state energy. The selection in set No. VI of the angular terms $(2p)^2$, $(3p)^2$, and $(3d)^2$ in favor of radial terms leads here to a substantial improvement of the convergence.

Granted that radial and angular terms are both

Table 12. Ground state energies and eigen vectors; Basis Sets I and VI.

Basis Set I		Basis Set VI	
$E_o = -2.8785974$		$E_o = -2.8997821$	
$\eta = 2.005$		$\eta = 2.325$	
c_{io}	config'n	c_{io}	config'n
0.9612	$(1s)^2$	0.9029	$(1s)^2$
-0.2546	1s2s	-0.3940	1s2s
0.1005	1s3s	0.1517	1s3s
-0.0322	$(2s)^2$	0.0631	$(2p)^2$
-0.0080	1s4s	-0.0304	1s4s
0.0052	2s4s	0.0272	$(2s)^2$
-0.0049	$(3s)^2$	0.0199	2s3s
0.0034	2s3s	-0.0137	$(3d)^2$
-0.0026	$(4s)^2$	0.0127	$(3p)^2$
-0.0015	3s4s	0.0081	2s4s

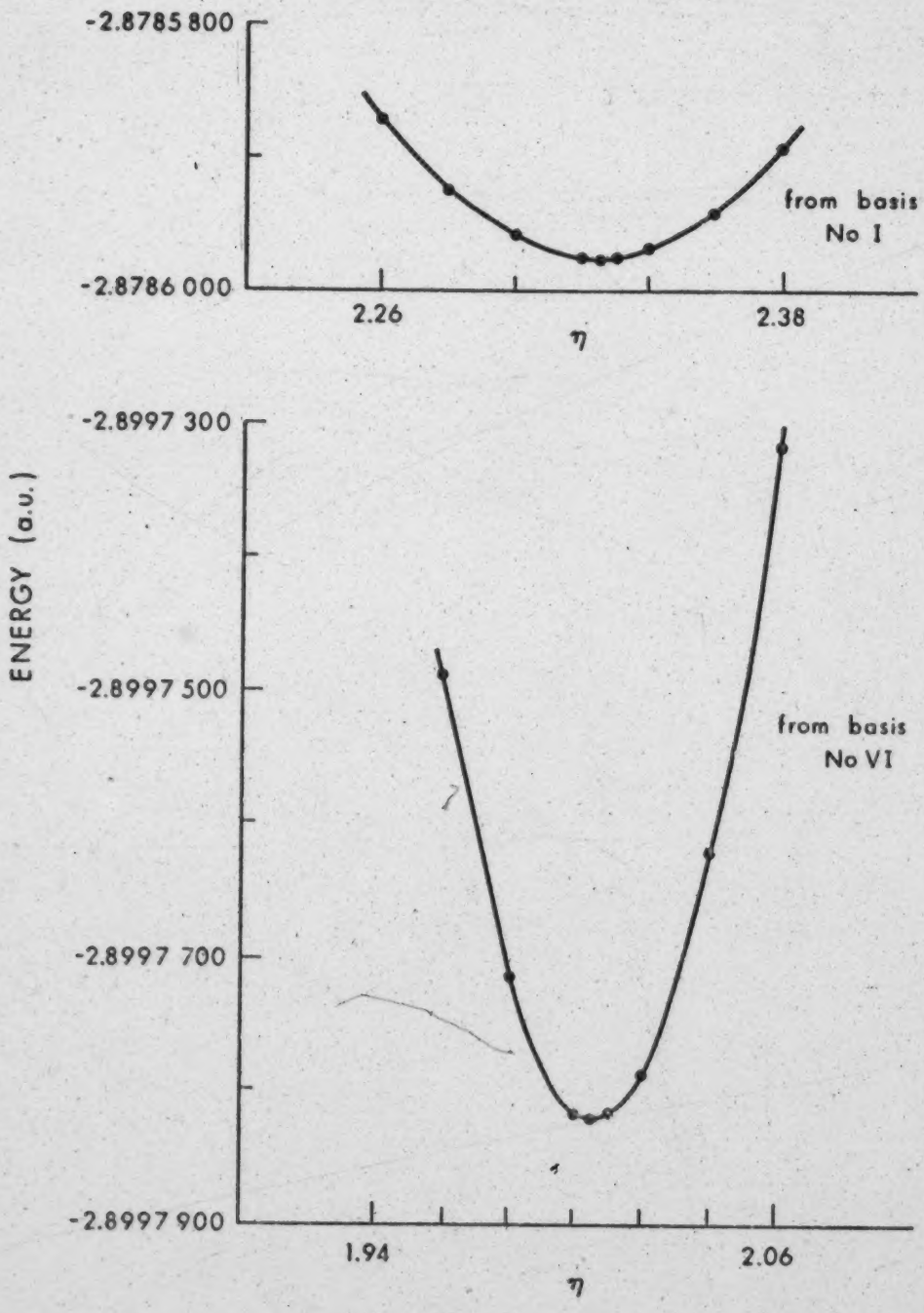

Figure 7. E_o minimization for He.

important, it is the sequencing of these which is crucial to optimize convergence. In the absence of physical considerations to choose a sequence, the results with sets No. I and VI suggest an alternative. If a truncated basis is to be developed by trial and error then after each trial the configurations dominant in the trial function should be retained and the remaining configurations should be replaced by untried ones for the next trial.

All trials, including those just described, with orthonormal bases, that is, with sets expressed in Laguerre orbitals and one orbital exponents, are summarized in Table 13. Some of the results are noteworthy.

The importance of angular correlation in the ground state was illustrated above with the two ten-term bases No. I and VI. Further confirmation is given by the fact, shown in Table 13, that basis No. VI with 10 terms gives a ground state energy practically as good as basis No. IV with 20 terms. Interestingly, the $(3d)^2$ term in basis No. VI is as effective as the eleven radial and angular terms in basis No. IV: $(3s)^2$, 3s4s, $(4s)^2$, 1s5s, 2s5s, 3s5s, 4s5s, $(5s)^2$, 2p3p, 2p4p, and 3p4p.

On the other hand, for the excited states, the radial terms in the bases are more important. This is

Table 13. E_k minimizations

	Optimal η	E_k	Basis Set No.	Configurations*	Length
k=0	2.005	-2.8786	I	$(1s)^2 \rightarrow (4s)^2$	10
	2.325	-2.8998	VI	$(1s)^2$,1s2s,$(2s)^2$, 1s3s,2s3s,1s4s,2s4s, $(2p)^2$,$(3p)^2$,$(3d)^2$	10
	2.350	-2.8998	IV	$(1s)^2 \rightarrow (5s)^2$,$(2p)^2$ $\rightarrow$ 3p4p	20
	2.222	-2.9012	III	$(1s)^2 \rightarrow (4s)^2$,$(2p)^2$ $\rightarrow (4f)^2$	20
	(exact:	-2.9037)			
k=1	1.08	-2.1336	III	$(1s)^2 \rightarrow (4s)^2$,$(2p)^2$ $\rightarrow (4f)^2$	20
	1.03	-2.1420	IV	$(1s)^2 \rightarrow (5s)^2$, $(2p)^2$ $\rightarrow$ 3p4p	20
	2.00	-2.1434	V	$(1s)^2 \rightarrow$ 1s15s	15
	(exact:	-2.1459)			
k=2	0.80	-1.9286	III	$(1s)^2 \rightarrow (4s)^2$,$(2p)^2$ $\rightarrow (4f)^2$	20
	0.80	-2.0243	IV	$(1s)^2 \rightarrow (5s)^2$,$(2p)^2$ $\rightarrow$ 3p4p	20
	1.95	-2.0464	V	$(1s)^2 \rightarrow$ 1s15s	15
	(exact:	-2.0613)			
k=3	0.70	-1.6377	III	$(1s)^2 \rightarrow (4s)^2$,$(2p)^2$ $\rightarrow (4f)^2$	20
	1.85	-1.9457	V	$(1s)^2 \rightarrow$ 1s15s	15
	(exact:	-2.0336)			

Table 13. (con't)

	Optimal			Basis Set	
	η	E_k	No.	Configurations*	Length
k=4	0.70	-0.7732	III	$(1s)^2 \rightarrow (4s)^2, (2p)^2 \rightarrow (4f)^2$	20
	1.70	-1.8119	V	$(1s)^2 \rightarrow 1s15s$	15
	(exact:	-2.0211)			

* A short hand notation refers to the sets given in Table 10.

seen in Table 13 by comparing E_o, E_1, and E_2 obtained from bases No. III and IV. The change from basis No. III to basis No. IV is equivalent to the replacement of the five angular configurations $(4p)^2$, $(3d)^2$, 3d4d, $(4d)^2$, and $(4f)^2$ by the radial terms 1s5s, 2s5s, 3s5s, 4s5s, and $(5s)^2$. The result is that E_1 improves from -2.1336 to -2.1420 a.u. and E_2 from -1.9286 to -2.0243 a.u. The improvement is, however, at the expense of the ground state: E_o changes from -2.9012 to -2.8998 a.u., consistent with the importance of angular correlation in the ground state discussed above.

To follow the role of radial terms further a basis was then chosen in which angular correlation was left out entirely. This is basis No. V: $(1s)^2$, 1s2s, 1s3s, ... 1s15s. Apart from the first term, it consists of only singly excited state configurations of the form 1sns. This choice is seen in Table 13 to bring a drastic improvement which is the greater the higher the excited state: E_1, E_2, E_3, and E_4 obtained with basis No. III improve respectively by 0.01, 0.02, 0.3, and 1.0 a.u.

The bases discussed up to this point all contain the restriction that the same variational value was assigned to all orbital exponents of one basis. Although further improvement would result from lengthening this

type of basis, greater efficiency should be obtainable by lifting the restriction to a common orbital exponent. Thus different values were chosen for the orbital exponents of basis No. III.

For the $(1s)^2$ configuration the orbital exponents $\eta_1 = 2.18$ and $\eta_2 = 1.19$ were chosen. These are the optimized exponents in Eckart's variation function (3,11) recognizing the radial correlation between the electrons in the ground state of helium. For the (1sns) configurations ($n \neq 1$) all 1s orbitals were assigned $\eta_1 = 2.0$ and all ns orbitals $\eta_2 = 1/n$. This basis is conveniently called the 1/n basis. With a configuration represented by $(n_1 s^{\eta 1}, n_2 s^{\eta 2})$ the basis can be written as:

$$(1s^{2.18}{}_{1s}{}^{1.19}), (1s^{2.0}{}_{2s}{}^{1/2}), (1s^{2.0}{}_{3s}{}^{1/3}), \ldots (1s^{2.0}{}_{15s}{}^{1/15})$$

The 1/n basis is also listed in Table 15 for later purposes.

All preceding bases were orthogonal since the associated Laguerre functions used as basis functions are orthogonal if they have the same orbital exponent (Chapter II). Since this advantage of orthogonality was lost in the 1/n set the Laguerre functions were replaced by the simpler Slater type orbitals (Chapter II).

Since in the 1/n basis all orbital exponents are

fixed only a linear variation can be applied. The resulting E_k values are listed in Table 14 and there compared with accurate values W_k. It is clear that the 1/n basis has led to a dramatic improvement.

The upper bounds agree with the Pekeris values to within the third rounded off decimal from the 4th ^1S state upward. To the best of the author's knowledge this is the first time that such close upper bounds were obtained by the CI method.

The conclusion is that these results firmly establish the great potential of the Rayleigh-Ritz variational method for excited states of two electron systems. The results suggest also that it will be worthwhile to investigate the application of the method to excited states of systems with three and more electrons.

IV.3 The 1/n basis versus the 0.08 basis

Under this heading a digression must now be made before the results obtained with the 1/n basis can be discussed in view of Wang and Weinhold's publication mentioned in the introduction. It was pointed out that the 1/n basis permits only linear variation, since all its orbital exponents have fixed values. A possible modification which permits some non-linear variation is the use of a common variable orbital exponent instead

of the fixed 1/n exponent.

Thus, the 1/n basis was modified by replacing only the orbital exponent $\eta_2 = 1/n$ by one variational value for η_2. This new basis is called the η_2 basis. Thus one has:

1/n basis:

$$(1s^{2.18}1s^{1.19}),(1s^{2.0}2s^{1/2}),(1s^{2.0}3s^{1/3}),\ldots(1s^{2.0}15s^{1/15})$$

and η_2 basis:

$$(1s^{2.18}1s^{1.19}),(1s^{2.0}2s^{\eta 2}),(1s^{2.0}3s^{\eta 2}),\ldots(1s^{2.0}15s^{\eta 2}).$$

The variation of η_2 of the new basis yielded minimization curves for each E_k in the same way as illustrated earlier for basis No. III in Figure 6. Except for E_o and E_1 all minimal E_k values were found at $\eta_2 = 0.08$. The η_2 basis with $\eta_2 = 0.08$, from here on called the 0.08 basis, is then the best η_2 basis for all k^{th} excited states for $k > 1$. The upper bounds obtained with the 0.08 basis are listed in Table 14 with those of the 1/n basis.

One notes immediately that the upper bounds from the 0.08 basis are even lower than those from the 1/n basis. A comparison with Pekeris values reveals however a discrepancy: as can be seen in the table, E_8 from the 0.08 basis is lower than the corresponding accurate

Table 14. Energies E_k of Excited ^1S States of Helium

k	W_k	1/n basis	0.08 basis	Wang and Weinhold (15)
0	-2.9037244 [a]	-2.8785254	-2.8758289	-2.95(11)
1	-2.1459533 [a]	-2.1422510	-2.1411445	-2.151(14)
2	-2.0612621 [a]	-2.0596102	-2.0598175	-2.0626(39)
3	-2.0335801 [a]	-2.0326995	-2.0330433	-2.0341(16)
4	-2.0211723 [a]	-2.0206640	-2.0209496	-2.02142(80)
5	-2.0145597 [a]	-2.0142508	-2.0144653	-2.01470(46)
6	-2.0106203 [a]	-2.0104283	-2.0105874	-2.01071(28)
7	-2.0080917 [a]	-2.0079655	-2.0080848	-2.00815(19)
8	-2.0063690 [a]	-2.0062851	-2.0063765	-2.00641(13)
9	-2.0051690 [b]	-2.0050869	-2.0051591	-2.005171(96)
10	--	-2.0042023	-2.0042615	-2.004200(72)
11	-2.0035838 [b]	-2.0035299	-2.0035815	-2.003036(43)

(a) References (23 and (24).

(b) References (17) and (23).

values of W_8. This E_k value is obviously not an upper bound and seems thereby to contradict the MacDonald theorem. But as mentioned in Chapter I this theorem is based on a rigorous proof that all E_k's obtained by the Rayleigh-Ritz variation must be upper bounds to the corresponding W_k's.

An explanation for this apparent contradiction was therefore sought in examining the accuracy of the computations involved. In the computational procedures, as described in Chapter II, three general stages can be distinguished.

i) the computations of the basic integrals in the setting up of the CI matrix.

ii) the canonical transformation to orthogonalize the matrix eigen value problem [Chapter II, equations (8) and (17)].

iii) the diagonalization of the transformed CI matrix.

Of these three the first and last could be ruled out as sources of large errors. In stage (i), in the calculation of the integrals no differencing errors occur since the expansions involved contain only additions. In stage (iii) the classic Jacobi diagonalization is applied and is well known to be very stable (22).

Errors could, however, be expected in the canonical transformation [stage (ii)]. It was realized that

replacing the values 1/n and 1/n' assigned to n in the orbital functions (ns) and n's) by one constant such as 0.08 will cause an increase of overlap between (ns) and (n's). For example, in the orbital notation of Chapter II:

$$\langle (5,0,0)\ n = 1/5 | (6,0,0)\ n = 1/6 \rangle = 0.8316$$

$$\langle (5,0,0)\ n = 0.08 | (6,0,0)\ n = 0.08 \rangle = 0.9574$$

Such an increase will affect the elements of the metric $\underset{\sim}{S}$ of the configuration basis, and may cause errors in the canonical transformation of $\underset{\sim}{S}$ according to:

$$\underset{\sim}{T}^t \underset{\sim}{S} \underset{\sim}{T} = \underset{\sim}{I} \qquad \text{[Chapter II, equation (13)]}.$$

An orthogonalization check was therefore applied by scanning the off-diagonal and diagonal elements of $\underset{\sim}{I}$ for deviations from respectively 0 and 1. The magnitude of the deviations should directly reflect the accuracy of the canonical orthogonalization. The following maximum deviations in I from the true identity matrix were found:

	diagonal elements	off-diagonal elements
0.08 basis	0.4097×10^{-3}	0.9500×10^{-3}
1/n basis	0.2873×10^{-9}	0.2265×10^{-7}

It is clear from these results that the choice of 0.08 for n_2 in the n_2 basis causes an impermissible inaccuracy in the orthogonalization. The failure of E_8 as an upper bound must therefore be ascribed to limitations of the computational precision. The 0.08 basis must therefore be rejected.

Another orthogonalization check, of importance for the discussion in the next section of Wang and Weinhold's work, is obtainable by investigating the orthogonalization of the orbital basis as distinct from the configuration basis. It was found that the Schmidt orthogonalized orbital functions yielded an overlap matrix which showed the following maximum deviations from a true identity matrix:

	diagonal elements	off-diagonal elements
0.08 basis	0.4128×10^{-2}	0.1205×10^{-1}
1/n basis	0.3317×10^{-8}	0.3845×10^{-8}

Again the 0.08 basis clearly causes serious computational errors. In anticipation of the discussion of Wang and Weinhold's work a difference between the orthogonalized orbitals of the 0.08 and the 1/n basis is noted here. An orthogonalized orbital function of

the 0.08 basis is an expansion in functions, most of which have the same orbital exponent, i.e., $\eta = 0.08$, whereas in the 1/n basis an orthogonalized orbital function is an expansion in functions with η defined differently for each function.

IV.4 Comparison with Wang and Weinhold's Excited States

Wang and Weinhold's work introduced at the beginning of this chapter can now be compared with the results with the 1/n basis. For direct comparison their results are listed with the present results in Table 14. Wang and Weinhold give the numbers in parentheses as the limits of error in the final two decimals. It is of interest to note that their average E_k values are all below the Pekeris values, exactly like the E_8 obtained from the 0.08 basis. The following discussion will show that these errors all have the same cause.

The difference between Wang and Weinhold's and the present work lies in the choice of the orbital functions. They chose the hydrogenic eigen functions instead of the Slater type orbitals (STO's). The hydrogenic eigen functions have the form of the Laguerre orbital functions given in Chapter II in which the orbital exponent η is replaced by Z/n; Z is the nuclear charge and n is the principal quantum number of the orbital concerned.

Their basis in terms of configurations and orbital exponents can then be written as:

$(1s^{2.0}1s^{2.0}),(1s^{2.0}2s^{1/2}),(1s^{2.0}3s^{1/3}),\ldots(1s^{2.0}ns^{1/n})$

and is quite similar to the 1/n basis which for comparison is repeated:

$(1s^{2.18}1s^{1.19}),(1s^{2.0}2s^{1/2}),(1s^{2.0}3s^{1/3}),\ldots(1s^{2.0}15s^{1/15}).$

Their bases consist of 25 configurations; the last term is $1s^{2.0}25s^{1/25}$.

Wang and Weinhold comment on the rather large errors given in the parentheses in the table, which they obtain while carrying out the calculations in double precision on an IBM 360/67, exactly as in the present work. They report that monitoring of the accumulation of errors shows up rather large differencing errors in the repulsion integrals between the Laguerre functions. As they state these errors can occur when, for large quantum numbers n, the oscillatory behavior of the wave functions becomes more and more pronounced.

With respect to the cause of these errors a similarity between Wang and Weinhold's basis and our 0.08 basis will now be discussed. The hydrogenic eigen functions can be expanded in STO's (16). Let $[n,\ell,m]^{1/n}$ represent the hydrogenic function with quantum numbers n,ℓ,m and orbital exponent 1/n and let $(n,\ell,m)^{1/n}$

represent a STO in a similar way. The expansion has the form:

$$[n,\ell,m]^{1/n} = \sum_{k=\ell+1}^{n} c_k \, [k,\ell,m]^{1/n}$$

Note that the orbital exponent of the STO's is 1/n and not 1/k. Thus the expansion generates (n-ℓ) STO's with the same orbital exponent 1/n. For example the orbital 25s is in fact a summation of 25 STO's, all with $\eta = 1/25$. It is this abundance of orbitals with the same η which caused the errors in the 0.08 basis, and is evidently also causing the errors in Wang and Weinhold's results.

It can therefore be concluded that the choice of Slater type orbitals for the 1/n basis represents a substantial improvement over Wang and Weinhold's choice of hydrogenic functions for their basis.

V. The CI functions for the ^1S states of Helium

V.1 Introduction

In the preceding chapter the E_k values were reported obtained with the Rayleigh-Ritz method applied to the 1/n basis. It remains now to report the corresponding CI functions for the n^1S states of He.

There are different ways to present a CI function Φ_k. The most direct one is as:

$$\Phi_k(1,2) = \sum_{k=1}^{N} c_{ik} \phi_i(1,2) \qquad (1)$$

since the c_{ik}'s are obtained as eigen vectors in the diagonalization of the CI matrix.

An alternative is the well known representation in natural orbitals (NO's) introduced by Löwden (18). The natural orbitals χ_{ik}^N are linear expansions in the one-electron basis functions, STO's in the present work. These expansions are obtained by a transformation such that the superposition of configurations constructed from the natural orbitals has the most rapid convergence. Further, in two-electron systems, the configurations are all doubly occupied orbitals. Thus the NO form of the CI function is

$$\Phi_k(1,2) = \sum_i a_{ik}^N \chi_{ik}^N(1) \chi_{ik}^N(2) \qquad (2)$$

with $a^{N}_{1k} > a^{N}_{2k} > a^{N}_{3k} > \ldots$ The transformation of the original STO basis to the NO basis has been derived by Löwden (18) in the context of the theory of density matrices. An alternative derivation (19) is given below in section V.2. This is of importance with respect to section V.3 in which "rational orbitals" will be introduced and derived.

The NO presentation for two-electron systems has been widely adopted because it ensures the most rapid convergence and also because the configurations being doubly occupied orbitals provide a description most suitable for ground states. But for singly excited states an expansion exclusively in doubly occupied orbitals does not seem to be the most "natural" or rather "rational" expression. Indeed from a chemical rather than a mathematical point of view one would prefer a rapidly converging expansion of Φ_k such that one configuration would be dominant and have singly occupied distinct orbitals χ^{R}_{1k} and χ^{R}_{2k} for the inner and outer electron. The expansion would then have the form:

$$\Phi_k(1,2) = a^{R}_{1k} \, [\chi^{R}_{1}(1) \; \chi^{R}_{2}(2)]^{*} + \ldots \qquad (3)$$

On the basis of these considerations Birss (19) has introduced the concept of "rational orbitals"

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*The square brackets will from here on refer to the symmetry adjusted form of the configuration.

(RO's). The development of this concept is given below, in section V.3, followed by an RO presentation of the CI functions obtained from the 1/n basis.

V.2 Natural Orbitals for Helium

The natural orbital expansion can be obtained by asking for that function of the form

$$\theta^N = [\chi_1^N \chi_1^N]^* \tag{1}$$

which has maximal overlap with the CI function

$$\Phi = \sum_{(k\ell)} a_{(k\ell)} [\chi_k \chi_\ell] \tag{2}$$

The expansion of the natural orbital, χ_1^N, in the basis functions for the CI function has the form

$$\chi_1^N = \sum_k \chi_k N_{k\ell} \tag{3}$$

so that

$$\theta^N = \sum_{(k\ell)} N_{k1} N_{\ell 1} [\chi_k \chi_\ell] \tag{4}$$

Assuming (without loss in generality) that the χ_i^N and the χ_i form orthonormal sets, one obtains the overlap

$$S = \langle \theta^N | \Phi \rangle = \sum_{(k\ell)} a_{(k\ell)} N_{k1} N_{\ell 1}$$

$$= \vec{N}_1^\dagger \underset{\sim}{a} \vec{N}_1 \tag{5}$$

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*Expressions such as $\chi_i \chi_j$ are from here on equivalent to $\chi_i(1)\chi_j(2)$.

with $\underline{a}$ the "fundamental matrix" of Löwdin (18).

To obtain natural orbitals S is maximized subject to the normalization constraint

$$\vec{N}_1^{\dagger}\,\vec{N}_1 = 1 \tag{6}$$

Using the method of undetermined multipliers (25) with multiplier ϵ, one has

$$(\delta\vec{N}_1^{\dagger})\,\underline{a}\,\vec{N}_1 + \vec{N}_1^{\dagger}\,\underline{a}\,(\delta\vec{N}_1) - [(\delta\vec{N}_1^{\dagger})\vec{N}_1 + \vec{N}_1^{\dagger}\,(\delta\vec{N}_1)] = 0 \tag{7}$$

or

$$(\delta\vec{N}_1^{\dagger})[\underline{a}\,\vec{N}_1 - \epsilon\vec{N}_1] + [\vec{N}_1^{\dagger}\,\underline{a} - \epsilon\vec{N}_1^{\dagger}](\delta\vec{N}_1) = 0$$

Since the two terms are mutually adjoint, it is adequate to take one term,

$$(\delta\vec{N}_1^{\dagger})[\underline{a}\,\vec{N}_1 - \epsilon\vec{N}_1] = 0 \tag{8}$$

Since $\delta\vec{N}_1^{\dagger}$ is an arbitrary variation, it follows that

$$\underline{a}\,\vec{N}_1 = \epsilon\vec{N}_1 \tag{9}$$

This equation is identical to that obtained by Löwden (18) showing that the maximum overlap criterion does obtain the natural orbitals for the two-electron problem.

V.3 "Rational" Orbitals for Helium

Consider the case where the natural orbital representation of a CI function is

$$\Phi = a_1^N [x_1^N x_1^N] + a_2^N [x_2^N x_2^N] \tag{1}$$

This appears to imply doubly occupied orbitals. Indeed if $|a_1^N| >> |a_2^N|$ a reasonable orbital approximation to the state is just $[x_1^N x_1^N]$ so that the natural orbitals are rational in this sense. If, however, a_1^N and a_2^N are of the same order of magnitude, either single determinant is a very poor approximation to the state.

Just such a situation arises when the best orbital approximation to the state is

$$Q^R = \frac{1}{\sqrt{2}} ([x_1^R x_2^R + x_2^R x_1^R]) \tag{2}$$

This can be seen by doing a natural orbital analysis on this function. The fundamental matrix is (assuming orthonormal orbitals)

$$\underline{a} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{3}$$

with eigen values

$$a_1^N = -a_2^N = \frac{1}{\sqrt{2}} \tag{4}$$

and eigenvectors

$$\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \qquad \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \tag{5}$$

i.e.,

$$\begin{aligned} x_1^N &= \frac{1}{\sqrt{2}} (x_1^R + x_2^R) \\ x_2^N &= \frac{1}{\sqrt{2}} (-x_1^R + x_2^R) \end{aligned} \tag{6}$$

Then

$$Q^R = \frac{1}{\sqrt{2}} [x_1^N \; x_1^N] - \frac{1}{\sqrt{2}} [x_2^N \; x_2^N] \tag{7}$$

Clearly (7) is an unnecessarily complicated expression of the "rational" form (2).

When a_1^N and a_2^N are unequal and close in magnitude, it is more rational to attempt to express the CI function in a series with (2) being the dominant term. The means to this is now sought initially in the context of a two-term natural orbital expansion as in (1).

Define

$$\begin{aligned} x_1^R &= R_{11} \, x_1^N + R_{21} \, x_2^N \\ x_2^R &= R_{12} \, x_1^N + R_{22} \, x_2^N \end{aligned} \tag{8}$$

Since (without loss in generality) the χ_i^N and χ_i^R can be assumed to form orthonormal sets in themselves, the matrix R is orthogonal and can be written as,

$$R = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \qquad (9)$$

The criterion for obtaining θ is to choose it such that Q^R, as defined in (2), shall have maximum overlap with ϕ, as defined in (1). Substituting (8) in (2) one obtains

$$\begin{aligned} Q^R = \frac{1}{\sqrt{2}}\{ & [(R_{11}\chi_1^N + R_{21}\chi_2^N)(R_{12}\chi_1^N + R_{22}\chi_2^N)] \\ & + [(R_{12}\chi_1^N + R_{22}\chi_2^N)(R_{11}\chi_1^N + R_{21}\chi_2^N)]\} \\ = \sqrt{2}\, & R_{11}R_{12}[\chi_1^N\chi_1^N] + \sqrt{2}\, R_{21}R_{22}\,[\chi_2^N\chi_2^N] \\ & + (R_{11}R_{22} + R_{21}R_{12})\,\frac{1}{\sqrt{2}}\,\{[\chi_1^N\chi_2^N] + [\chi_2^N\chi_1^N]\} \end{aligned} \qquad (10)$$

Since the χ_i^N are an orthonormal set, the overlap is

$$S = \langle Q^R | \phi \rangle = \sqrt{2}\,(a_1^N R_{11}R_{12} + a_2^N R_{21}R_{22}) \qquad (11)$$

Substitution of the elements of R as in equation (9) yields

$$\begin{aligned} S &= \sqrt{2}\,\sin\theta\cos\theta\,(a_2^N - a_1^N) \\ &= \frac{1}{\sqrt{2}}\,(a_2^N - a_1^N)\sin 2\theta \end{aligned} \qquad (12)$$

Maximizing S by

$$\frac{dS}{d\theta} = 0 = \sqrt{2}\ (a_2^N - a_1^N)\ \cos 2\theta \tag{13}$$

one obtains

$$\theta = \frac{\pi}{4} \tag{14}$$

so that

$$\underset{\sim}{R} = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \tag{15}$$

Thus the relation between rational and natural orbitals is

$$\begin{aligned} x_1^R &= \frac{1}{\sqrt{2}}\ (x_1^N + x_2^N) \\ x_2^R &= \frac{1}{\sqrt{2}}\ (-x_1^N + x_2^N) \end{aligned} \tag{16}$$

so that

$$\begin{aligned} x_1^N &= \frac{1}{\sqrt{2}}\ (x_1^R - x_2^R) \\ x_2^N &= \frac{1}{\sqrt{2}}\ (x_1^R + x_2^R) \end{aligned} \tag{17}$$

Substituting (17) in (1) one has

$$\Phi = \frac{1}{2} a_1^N [(x_1^R - x_2^R)(x_1^R - x_2^R)] + \frac{1}{2} a_2^N [(x_1^R + x_2^R)(x_1^R + x_2^R)]$$

$$= \frac{1}{\sqrt{2}} (a_2^N - a_1^N) \frac{1}{2} \{[x_1^R x_2^R] + [x_2^R x_1^R]\}$$

$$+ \frac{1}{2} (a_1^N + a_2^N) [x_1^R x_1^R] + \frac{1}{2} (a_1^N + a_2^N) [x_2^R x_2^R] \qquad (18)$$

Expressing this in rational form as

$$\Phi = a_{12} \frac{1}{\sqrt{2}} \{[x_1^R x_2^R] + [x_2^R x_1^R]\} + a_{11} [x_1^R x_1^R] + a_{22} [x_2^R x_2^R] \qquad (19)$$

one obtains

$$a_{12}^R = \frac{1}{\sqrt{2}} (a_2^N - a_1^N)$$

$$a_{11}^R = a_{22}^R = \frac{1}{\sqrt{2}} (a_1^N + a_2^N) \qquad (20)$$

Where does the natural orbital analysis "go wrong", in the sense that it gives a function which is practically correct but analytically obscure?

By the very act of diagonalizing the fundamental matrix one forces the expression of a CI function into a series of doubly occupied orbital configurations. What was done in the previous section was to "dis-diagonalize" the matrix, using as criterion the requirement to maximize the off-diagonal element. To accomplish

the goal of obtaining a function which is analytically clear while containing some minimal number of terms, one wishes to transform the fundamental matrix so that it is zero everywhere except for a minimal block centred on the diagonal (thus ensuring use of a minimal set of χ_i^R in expressing the function) and to have one off-diagonal element in that block as large as possible.

This procedure is ill-defined because it does not specify a way to obtain a minimal block. But the natural orbital analysis does specify a way to a minimal block (albeit diagonal): diagonalize the fundamental matrix. Then the process of "dis-diagonalization" can proceed to obtain satisfaction of the other criterion.

The procedure for "dis-diagonalization" should be examined in some detail. Assume that the diagonalized matrix

$$\underset{\sim}{a}^{(0)} = \begin{pmatrix} a_{11}^{(0)} & 0 & 0 & \cdots \\ 0 & a_{22}^{(0)} & 0 & \cdots \\ 0 & 0 & a_{33}^{(0)} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} \tag{21}$$

is arranged with

$$|a_{11}^{(0)}| \geq |a_{22}^{(0)}| \geq |a_{33}^{(0)}| \geq \cdots \tag{22}$$

Select a_{12} as the element to be maximized by an orthogonal transform of $a^{(0)}$. This can generally be accomplished by applying successive orthogonal transformations of the form

$$T^{(mn)} = \begin{pmatrix} 1 & & & & & & \\ & \ddots & & & & & \\ & & 1 & & & & \\ & & & \cos\theta & & -\sin\theta & \\ & & & & 1 & & \\ & & & & & \ddots & \\ & & & & & & 1 \end{pmatrix} \begin{matrix} \\ \\ m \\ \\ \\ n \\ \\ \end{matrix}$$

with θ chosen such as to maximize the a_{12} element. Such a transformation can alter the value of the a_{12} element only if m = 1 or 2 or n = 1 or 2. Thus the chosen transformations must be one of $T^{(12)}$, $T^{(13)}$, ..., $T^{(1n)}$, ... or $T^{(23)}$, $T^{(24)}$, ... , $T^{(2n)}$ ... .

Consider the effect of transformation $T^{(12)}$:

$$a^{(1)} = T^{(12)}\, a^{(0)}\, T^{(12)} \tag{24}$$

for which

$$a_{11}^{(1)} = a_{11}^{(0)} \cos^2 \theta + a_{22}^{(0)} \sin^2 \theta$$

$$a_{22}^{(1)} = a_{11}^{(0)} \sin^2 \theta + a_{22}^{(0)} \cos^2 \theta \qquad (25)$$

$$a_{12}^{(1)} = \sin \theta \cos \theta \, (a_{22}^{(0)} - a_{11}^{(0)})$$

Elements $a_{12}^{(1)}$ are maximized when $\theta = \frac{\pi}{4}$ so that

$$a_{11}^{(1)} = \frac{1}{2} (a_{11}^{(0)} + a_{22}^{(0)})$$

$$a_{22}^{(1)} = a_{11}^{(1)} \qquad (26)$$

$$a_{12}^{(1)} = \frac{1}{2} (a_{22}^{(0)} - a_{11}^{(0)})$$

$$a_{k\ell}^{(1)} = a_{k\ell}^{(0)}, \quad k,\ell > 2$$

$$a_{1\ell}^{(1)} = a_{2\ell}^{(1)} = 0, \quad \ell > 2$$

It can also be shown that if any other transformation is effected, the magnitude of a_{12} is decreased. Consider using transformation $T^{(1n)}$:

$$\underset{\sim}{a}^{(2)} = \underset{\sim}{T}^{(1n)} \, \underset{\sim}{a}^{(1)} \, \underset{\sim}{T}^{(1n)}$$

for which

$$a_{12}^{(2)} = a_{12}^{(1)} \cos \theta \qquad (27)$$

Clearly $a_{12}^{(2)}$ remains with its maximum magnitude

only if cos θ = 1, i.e., $\underset{\sim}{T}^{(n)}$ must be, trivially, the unit matrix. Using transformation $\underset{\sim}{T}^{(2n)}$ one has

$$a_{12}^{(2)} = a_{12}^{(1)} \cos \theta \qquad (28)$$

with the same result. Thus, regardless of the number of natural orbitals in the minimal block, the only transformation to rational form is that on the pair of natural orbitals R or t for which $|a_k^N - a_t^N|$ is a maximum.

V.4 The CI functions for the 1sns ^1S states of He.

The CI functions are discussed below in terms of Slater type orbitals (STO's), natural orbitals (NO's) and rational orbitals (RO's). The 1/n basis is detailed in Table 15 to provide a reference for the configuration and orbital numbers used in Tables 16, 18, 19 and 20.

i) The STO presentation.

In Table 16 the CI functions are represented by the coefficients in the expansion

$$\phi_k(1,2) = \sum_{i=1}^{15} c_{ik} \phi_i(1,2)$$

in which the ϕ_i's are the non-orthogonal ^1S functions

of the configurations, listed in Table 15, expressed in STO's. This representation is obtained directly from the Rayleigh-Ritz method.

ii) The NO presentation.

Since the RO presentation is preferred over the NO presentation and therefore will be given below in full, a few examples of the NO presentations will suffice. Some examples, in terms of the coefficients in the normalized natural expansion,

$$\phi_k(1,2) = \sum_i \left[a_{ik}^N \chi_{ik}^N(1) \chi_{ik}^N(2) \right],$$

are

i	a_{i0}^N	a_{i3}^N	a_{i7}^N	a_{i12}^N
1	0.997840	0.725600	0.713048	0.709976
2	-0.656914	-0.688102	0.701114	-0.704226
3	0.000364	0.000205	-0.001492	-0.000699

It is noted that only the ground state has a coefficient close to 1 for the first doubly occupied NO. The nearly equal weighting of the first two con-

figurations in Φ_3, Φ_7, and Φ_{12} is typical for all Φ_k's ($k > 0$) obtained.

iii) The RO presentation.

The expansion coefficients in the rational expansion

$$\Phi_k = a^R_{1k} \frac{1}{\sqrt{2}} (\chi^R_{1k}\chi^R_{2k} + \chi^R_{2k}\chi^R_{1k}) + a^R_{2k}\chi^R_{1k}\chi^R_{1k} + a^R_{3k}\chi^R_{2k}\chi^R_{2k} + \ldots$$

are presented in Table 17. The advantage of the RO presentation over the NO presentation is evident from the table: in all excited state functions the first configuration, dominant by a coefficient very close to 1, describes the inner and outer electron with distinct orbitals. The rapid convergence is also noted: all CI coefficients not listed are smaller than 0.001.

As seen in the second column of the table the CI coefficients a^R_{ik} of the dominant configurations increase with higher excited state. An exception is the coefficient for the 15^1S state which is down to -0.996196 from the preceding value of 0.999991 for the 14^1S state. This breakdown in the upward trend can be expected from a comparison of the following E_k values belonging to the CI functions.

$$E_{12} = -2.0035 \text{ a.u.}$$

$$E_{13} = -2.0030 \text{ a.u.}$$

$$E_{14} = -2.0026 \text{ a.u.}$$

$$E_{15} = -1.9678 \text{ a.u.}$$

There is clearly a corresponding breakdown in the goodness of these upper bounds, the interval between E_{14} and E_{15} being about 100 times larger than those between E_{12}, E_{13}, and E_{14}. Since E_{15} lies well above the series limit of -2.00 a.u. for the isns ^1S series, the corresponding trial function and CI coefficients can safely be left out for further consideration.

The increase of a_{ik}^R with higher states signifies that in the CI function Φ_k the energy contribution of the dominant configuration of the form $[x_1 x_2]$ to the exact state energy is progressively more the higher k in Φ_k. This implies that progressively less of the exact energy is to be accounted for by superposition of configurations. Thus the CI functions obtained, as expressed in RO's, clearly reflect the expectation that less correlation energy is to be accounted for the further the outer electron is on the average away from the inner electron.

V.5 The Rational Orbital Functions

In this section the expansion coefficients of the rational orbitals χ^R_{1k} and χ^R_{2k} are examined for their physical content. Let the one-electron basis functions (STO's) of the 1/n basis be represented by $f_1, f_2, \ldots f_{17}$ corresponding to the order in which they are listed in Table 15. As stated above the RO's are presented in Table 18 and 19 on an orthogonal basis. This basis, to be called $F_1, F_2, \ldots F_{17}$ was obtained by Schmidt-orthogonalization of $f_1, f_2, \ldots f_{17}$. It is here important to recall that the Schmidt-orthogonalization is an upper triangular one. Thus

$$F_k = \sum_{i=1}^{k} a_{ik} f_i \qquad (1)$$

and this implies that a progression along $F_1, F_2, \ldots F_{17}$ entails a progressive incorporation of f_k's in the expansion of F_k. Since the f_k's are STO's ordered with increasing principal quantum number and correspondingly decreasing orbital exponent such a progression would describe an electron progressively further away from the nucleus on the average. Consequently if in the expansion of a rational orbital such as

$$\chi^R_k = \sum_{i=1}^{17} b_{ik} F_i \qquad (2)$$

the highest coefficient would change from b_{im} to b_{in} with $n > m$, this change would correspond to an increase of the average distance of the electron from the nucleus.

In the light of above analysis the RO's can now be examined. They are presented in Table 18 and 19 as columns of the expansion coefficients b_{ik}, which according to equation (2) correspond to the orthogonalized STO's F_i. Each RO can be characterized by its dominant coefficient b_{ik}, to be selected from the tables, and corresponding F_k. The results are listed in Table 20.

It is seen in the table that the inner electron is consistently described by orbital no. 1, that is F_1. According to the Schmidt-orthogonalization F_1 is f_1: the 1s STO with orbital exponent $\eta = 2.00$ (Table 15) and this is the exact wave function for the He^+ ion. The coefficients of this orbital are seen, in column 2 of the table, to increase as the state described becomes higher. This means that as the CI function describes a higher state, the RO for the inner electron comes closer to the description of an electron in a He^+-like environment, implying correspondingly less correlation energy between the two electrons. This supports the conclusion, reached above in the discussion of the dominant CI coefficients,

Table 15 The 1/n basis

Basis orbitals: $(ns^n) = r^{n-1}e^{-nr}$ (STO's)

Configurations		STO's		
No	STO's	No	n	n
1	2 3	1	1	2.00
2	1 4	2	1	2.18
3	1 5	3	1	1.19
4	1 6	4	2	1/2
5	1 7	5	3	1/3
6	1 8	6	4	1/4
7	1 9	7	5	1/5
8	1 10	8	6	1/6
9	1 11	9	7	1/7
10	1 12	10	8	1/8
11	1 13	11	9	1/9
12	1 14	12	10	1/10
13	1 15	13	11	1/11
14	1 16	14	12	1/12
15	1 17	15	13	1/13
		16	14	1/14
		17	15	0.07

Note: n in orbital 17 was set to 0.07 instead of 1/15 = 0.06̄ to prevent exponential overflow in the computation of the metrix matrix of the configuration basis.

Table 16 CI functions Φ_k in STO's (non-orthogonal configuration basis)

Config.	c_{i0}	c_{i1}	c_{i2}	c_{i3}	c_{i4}
1	0.758994	0.285464	0.163499	0.106776	-0.075364
2	-0.029045	-0.943451	-0.638236	-0.439121	-0.315811
3	0.007368	-0.386846	0.324971	0.354027	0.279885
4	0.007626	0.923361	2.251544	1.188296	1.593017
5	-0.036726	-1.926819	-4.247175	-6.658906	-7.122363
6	0.091696	3.696115	7.775960	11.244687	15.153673
7	-0.182460	-6.450293	-13.239400	-18.480520	-23.059667
8	0.308277	10.085090	20.402244	27.960975	33.761809
9	-0.446437	-13.886390	-27.836076	-37.745522	-44.805620
10	0.549502	16.504974	32.882947	44.294195	52.060013
11	-0.564348	-16.526669	-32.785335	-43.969893	-51.357954
12	0.471088	13.536055	26.769427	35.793742	41.635740
13	-0.311281	-8.815092	-17.393011	-23.206798	-26.917819
14	0.169086	4.736659	9.330308	12.430523	14.390417
15	-0.057451	-1.601188	-3.151611	-4.196011	-4.853454

(continued)

Table 16 (con't)

Config.	c_{i5}	c_{i6}	c_{i7}	c_{i8}	c_{i9}
1	-0.056129	0.043516	0.034814	-0.028576	-0.023976
2	0.236386	-0.182908	-0.145446	0.188312	0.098126
3	-0.205120	0.145469	0.099999	-0.065236	-0.038002
4	-1.405579	1.278091	1.186924	-1.129036	-1.075490
5	6.973528	-6.662642	-6.338496	6.055167	5.837359
6	-17.311316	18.303017	18.690726	-18.820742	-18.909343
7	28.998581	-34.176421	-38.263396	41.548446	44.452273
8	-39.335288	47.854001	57.880446	-68.414131	-79.303574
9	50.548405	-56.797548	-68.303916	85.490892	107.84513
10	-57.755987	62.779767	69.107574	-83.725448	-110.97502
11	56.419667	-60.276191	063.974893	69.596888	87.296139
12	-45.455424	48.070364	50.062042	-52.115929	-56.431503
13	29.265655	-30.749687	-31.668969	32.229312	32.851184
14	-15.602510	16.325647	16.699661	-16.779658	-16.598870
15	5.255983	-5.489903	-5.600014	5.598865	5.478715

(continued)

Table 16 (con't)

Config.	c_{i10}	c_{i11}	c_{i12}	c_{i13}	c_{i14}
1	-0.020532	0.017985	0.016296	-0.016308	-0.426658
2	0.082846	-0.071318	-0.063255	0.061564	2.287963
3	-0.015781	-0.003475	-0.021821	0.045392	-7.190218
4	-1.050171	1.049343	1.088061	-1.259903	18.233996
5	5.705647	-5.694591	05.891280	6.801234	-40.575258
6	-19.122764	19.653168	20.871703	-24.702401	80.785283
7	47.443287	-51.138225	-56.709813	69.957254	-143.95438
8	-91.052294	104.88635	123.62365	-161.67685	227.74177
9	135.58984	-170.58847	-218.36740	309.14966	-315.69286
10	-153.81665	216.59811	309.74830	-488.13614	376.65757
11	128.79692	-207.29223	-344.10906	628.27798	-377.95915
12	-77.707532	141.07194	286.39345	-644.81001	309.92055
13	35.989448	-63.241576	-166.35347	515.05326	-201.94301
14	-16.513797	19.902325	63.073697	-330.40047	108.53400
15	5.279261	-5.629264	-12.944264	122.81037	-36.689985

Table 17 CI functions Φ_k in RO's

Coefficients →	a^R_{1k}	a^R_{2k}	a^R_{3k}	a^R_{4k}
Configuration →	1st	2nd	3rd	4th
RO's →	1 2	1 1	2 2	3 3
Φ_0 for 1^1S :	---	0.997840 (a)	-0.065691 (b)	0.000364 (c)
Φ_1 for 2^1S:	0.996454	0.059004	0.059004	-0.010772
Φ_2 for 3^1S:	0.999081	0.029921	0.029921	-0.006799
Φ_3 for 4^1S:	0.999638	0.018749	0.018749	-0.004526
Φ_4 for 5^1S:	0.999825	0.013012	0.013012	-0.003215
Φ_5 for 6^1S:	0.999904	-0.009626	-0.009626	0.002401
Φ_6 for 7^1S:	0.999943	0.007450	0.007450	-0.001864
Φ_7 for 8^1S:	0.999963	0.005967	0.005967	-0.001492
Φ_8 for 9^1S:	0.999975	0.004913	0.004913	0.001225
Φ_9 for 10^1S:	-0.999982	-0.004140	-0.004140	0.001028
Φ_{10} for 11^1S:	-0.999987	-0.003566	-0.003566	0.000881
Φ_{11} for 12^1S:	0.999990	0.003146	0.003146	-0.000771
Φ_{12} for 13^1S:	0.999991	0.002875	0.002875	-0.000699
Φ_{13} for 14^1S:	0.999991	-0.002909	-0.002909	0.000700
Φ_{14} for 15^1S:	-0.996196	-0.060614	-0.060614	0.015656

(continued)

Table 17. References

(a) Coefficient a_{10}^{R} of the 1st configuration

(b) Coefficient a_{20}^{R} of the 2nd configuration

(c) Coefficient a_{30}^{R} of the 3rd configuration

Table 18 Rational Orbitals χ^{R}_{ik}

i	b_{i0}	b_{i1}	b_{i2}	b_{i3}	b_{i4}
1	0.983706	0.999065	-0.999771	0.999911	-0.999957
2	-0.159428	-0.015463	0.004436	-0.001807	0.000884
3	0.082813	0.024258	-0.005297	0.001969	-0.000927
4	-0.006266	0.032217	0.005054	-0.001746	0.000808
5	0.002475	-0.000489	0.019436	0.000542	-0.000279
6	-0.001200	-0.000314	0.001391	0.012557	-0.000686
7	0.000613	0.000477	-0.001052	0.002197	0.008515
8	-0.000295	-0.000523	0.000853	-0.001256	0.002502
9	0.000105	0.000534	-0.000736	0.000885	-0.001240
10	0.000017	-0.000531	0.000660	-0.000701	0.000802
11	-0.000009	0.000523	-0.000607	0.000594	-0.000599
12	0.000156	-0.000512	0.000568	-0.000526	0.000489
13	-0.000196	0.000501	-0.000537	0.000480	-0.000422
14	0.000226	-0.000490	0.000513	-0.000446	0.000378
15	-0.000248	0.000478	-0.000493	0.000421	-0.000348
16	0.000264	-0.000468	0.000475	-0.000401	0.000326
17	-0.000305	0.000504	-0.000506	0.000423	-0.000340

(continued)

Table 18 (con't)

i	b_{i5}	b_{i6}	b_{i7}	b_{i8}	b_{i9}
1	0.999977	-0.999986	0.999991	0.999994	0.999996
2	-0.000487	0.000292	-0.000188	-0.000127	-0.000090
3	0.000502	-0.000299	0.000192	0.000130	0.000092
4	-0.000435	0.000259	-0.000166	-0.000113	-0.000080
5	0.000163	-0.000102	0.000067	0.000047	0.000034
6	0.000251	-0.000117	0.000063	0.000037	0.000024
7	-0.000993	0.000435	-0.000234	-0.000142	-0.000093
8	0.005968	-0.000995	0.00478	0.000276	0.000176
9	0.002570	0.004274	-0.000894	-0.000460	-0.000280
10	-0.001135	0.002525	0.003100	0.000761	0.000415
11	0.000684	-0.000999	0.002426	-0.002262	-0.000627
12	-0.000488	0.000562	-0.000855	-0.002302	0.001649
13	0.000386	-0.000384	0.000448	0.000713	0.002170
14	-0.000327	0.000297	-0.000294	-0.000344	-0.000578
15	0.000290	-0.000249	0.000223	0.000217	0.000252
16	-0.000265	0.000220	-0.000186	-0.000163	-0.000151
17	0.000273	-0.000220	0.000180	0.000148	0.000122

(continued)

Table 18 (con't)

i	b_{i10}	b_{i11}	b_{i12}	b_{i13}	b_{i14}
1	0.999997	0.999998	0.999998	0.999998	0.998949
2	-0.000066	-0.000051	0.000043	-0.000043	-0.022650
3	0.000069	0.000054	-0.000045	0.000047	0.016612
4	-0.000060	-0.000047	0.000039	-0.000041	-0.013575
5	0.000026	0.000021	-0.000018	0.000019	0.006223
6	0.000016	0.000011	-0.000009	0.000008	-0.000227
7	-0.000065	-0.000048	0.000038	-0.000038	-0.004033
8	0.000122	0.000090	-0.000072	0.000071	0.006899
9	-0.000188	-0.000014	0.000108	-0.000106	-0.008760
10	0.000266	0.000188	-0.000147	0.000143	0.009922
11	-0.000362	-0.000245	0.000187	-0.000179	-0.010606
12	0.000504	0.000310	-0.000227	0.000214	0.010964
13	-0.001195	-0.000398	0.000267	-0.000243	-0.011100
14	-0.002040	0.000857	-0.000313	0.000263	0.011085
15	0.000450	0.001926	0.000608	-0.000273	-0.010968
16	-0.000169	-0.000327	0.001850	0.000446	0.010786
17	0.000101	0.000095	-0.000201	0.001926	-0.011614

Table 19 Rational Orbitals χ_{2k}^{R}

i	b_{i0}	b_{i1}	b_{i2}	b_{i3}	b_{i4}
1	0.178093	-0.042844	0.021325	-0.013301	0.009216
2	0.927263	-0.231107	0.128694	-0.083093	0.058393
3	-0.328794	0.570573	-0.238755	0.140186	-0.094616
4	0.017231	0.785709	0.240163	-0.131986	0.087938
5	-0.006807	-0.011920	0.923654	0.040982	-0.030401
6	-0.003299	-0.007577	0.066107	0.949345	-0.074673
7	-0.001686	0.011621	-0.050009	0.166110	0.926545
8	0.000813	-0.012762	0.040514	-0.094954	0.272222
9	-0.000289	0.013022	-0.034964	0.066940	-0.134877
10	-0.000046	-0.012952	0.031375	-0.052998	0.087232
11	0.000272	0.012748	-0.028860	0.044938	-0.065198
12	-0.000428	-0.012491	0.026991	-0.039791	0.053171
13	0.000540	0.012215	-0.025539	0.036266	-0.045873
14	-0.000621	-0.011938	0.024373	-0.033723	0.41109
15	0.000681	0.011669	-0.023409	0.031813	-0.037830
16	-0.000725	-0.011410	0.022594	-0.030326	-0.035471
17	0.000840	0.012281	-0.024066	0.032010	-0.037013

(continued)

Table 19 (con't)

i	b_{i5}	b_{i6}	b_{i7}	b_{i8}	b_{i9}
1	0.006813	0.005271	0.004221	0.003474	0.002928
2	0.043440	0.033696	-0.027000	0.022211	0.018688
3	-0.069102	-0.053185	0.042532	-0.035047	-0.029614
4	0.063973	0.049176	-0.039319	0.032412	0.027406
5	-0.023906	-0.019277	0.015933	-0.013473	-0.011638
6	-0.036958	-0.022189	0.014874	-0.010690	-0.008059
7	0.145906	0.082673	-0.055501	0.040757	0.031685
8	-0.877315	-0.188983	0.113341	-0.079343	-0.060229
9	-0.377779	0.811594	-0.211860	0.132389	0.095544
10	0.166891	0.479469	0.734050	-0.210229	-0.141943
11	-0.100496	-0.189704	0.575062	0.651227	0.214376
12	0.071681	0.106700	-0.202640	0.662863	-0.563423
13	-0.056726	-0.072986	0.106110	-0.205296	-0.741424
14	0.048048	0.056399	-0.069735	0.099107	0.197397
15	-0.042617	-0.047215	0.052911	-0.062515	-0.086058
16	0.039022	0.041705	-0.044079	0.046823	0.051740
17	-0.040078	-0.041858	0.042696	-0.042687	-0.041770

(continued)

Table 19 (con't)

i	b_{i10}	b_{i11}	b_{i12}	b_{i13}	b_{i14}
1	0.002522	-0.222445	0.002033	0.002057	0.044902
2	0.016058	-0.014122	0.012858	0.012947	0.311573
3	-0.025610	0.022715	-0.020904	-0.021340	-0.360473
4	0.023723	-0.021067	0.019415	0.019855	0.329020
5	-0.010269	0.009290	-0.008722	-0.009102	-0.150830
6	-0.006294	0.005064	-0.004218	-0.003850	0.005490
7	0.025679	-0.021578	0.018928	0.018449	0.097738
8	-0.048213	0.040283	-0.035291	-0.034483	-0.167209
9	0.074434	-0.061211	0.053121	0.051639	0.212312
10	-0.105365	0.084404	-0.072115	-0.069441	-0.240487
11	0.143673	-0.110070	0.091823	0.087190	0.257067
12	-0.200034	0.139314	-0.111671	-0.103881	-0.265742
13	0.474133	-0.178825	0.131295	0.118065	0.269033
14	0.809515	0.385526	-0.153742	-0.127823	-0.268666
15	-0.178506	0.866096	0.299038	0.132528	0.265843
16	-0.067004	-0.147200	0.910141	-0.216709	-0.261414
17	-0.040249	0.042918	-0.098687	-0.936304	0.281492

Table 20 Characterization of Rational Orbitals χ_k^R

n in	Dominant Orbitals F_i			
	inner electron		outer electron	
$(1sns)^1S$	Coeff.	i in F_i	Coeff.	i in F_i
1	0.98370577	1	0.984	1
2	0.99906525	1	0.786	4
3	0.99977111	1	0.924	5
4	0.99991128	1	0.949	6
5	0.99995747	1	0.927	7
6	0.99997677	1	-0.877	8
7	0.99998610	1	0.812	9
8	0.99999109	1	0.735	10
9	0.99999396	1	0.663	12
10	0.99999571	1	-0.741	13
11	0.99999682	1	0.810	14
12	0.99999753	1	0.866	15
13	0.99999793	1	0.910	16
14	0.99999788	1	0.936	17
15	0.99894875	1	?	?

that the RO presentation of the CI function clearly reflects the relative spatial orientation of the electrons.

As for the outer electron, there is, in Table 20, clearly a progression towards higher F_k with higher excited state. By the analysis given above of the Schmidt-orthogonalization this means that RO describes the outer electron as being on the average further away from the nucleus as n in 1sns ^1S increases.

In conclusion, the RO presentation of a two-electron CI function is in accordance with the chemist's picture of the inner electron being in a 1s He^+-like orbital. Also, as the state energy increases, the RO for the outer electron indicates that the electron is progressively further away on the average from the nucleus, and reflects the corresponding decrease in correlation energy.

VI. The $(2s)^2\,{}^1S$ State of Helium

VI.1 Introduction

Compton and Boyce (27) observed an emission line in the vacuum ultraviolet, a corona line, with wave number 279,715 cm^{-1}. Kruger identified this line with the transition $(2s)^2\,{}^1S$ - $1s2s\,{}^1S$ on the basis that, firstly, the line never occurred in helium spectra when another line, identified with the transition $(1s)^2\,{}^1S$ - $1s2s\,{}^1S$ was absent and that, secondly, the line fell within a calculated 20,000 cm^{-1} interval. No details of the calculations were given. Bransden and Dalgains (29) calculated on the basis of perturbation theory that the line may correspond to one of the transitions $2s2p\,{}^3P$ - $1s4s\,{}^3S$, $2s2p\,{}^3P$ - $1s5s\,{}^3S$ and $2s2p\,{}^3P$ - $1s4d\,{}^3D$.

If the $(2s)^2\,{}^1S$ - $1s2s\,{}^1S$ transition is the correct interpretation, the state energy of the $(2s)^2\,{}^1S$ state can be calculated as follows:

accurate energy of $1s2s\,{}^1S$;	-2.1469 a.u.
$(2s)^2\,{}^1S$ - $1s2s\,{}^1S$ transition:	
279,715 cm^{-1} =	1.2744 a.u.
energy of $(2s)^2\,{}^1S$ state:	-0.8716 a.u.

Holoien (26) has set out to test this interpretation by constructing a CI function for the $(2s)^2\ ^1S$ state. This function has an expectation value for the energy of -0.7985 a.u. On the basis of the difference between this value and the one calculated above, -0.8716 a.u., Holoien rejects the transition $(2s)^2\ ^1S - 1s2s\ ^1S$ as an interpretation of the corona line. Using his CI functions he calculates that other possible transition for the corona line are: $(2s)^2\ ^1S - 1s3p\ ^1P$ and $(2s)^2\ ^1S - 1s3p\ ^3P$. By implication Holoien claims that his CI function is a good approximation to the $(2s)^2\ ^1S$ state and that the energy of -0.7985 a.u. is a close upper bound to the true energy of that state. In the following sections these claims are, however, rejected.

VI.2 Holoien's CI function

In his work on the $(2s)^2\ ^1S$ state (26), one of the bases Holoien used to construct CI functions was basis No. III listed in Table 10. As described in Chapter IV it was this basis which in the present work was selected for an initial study of the Rayleigh-Ritz variational method. Of particular interest here is Figure 6 in which the results were plotted. There is complete agreement with Holoien calculations for the ground state:

the coefficients of the CI function Φ_o and the energy E_o are in the present work identical to those obtained by Holoien.

The main point, however, of Holoien's publication is the claim that with the same basis a good CI function is obtained for the $(2s)^2\ ^1S$ state. That function, listed as a vector of expansion coefficients, is stated to belong to a minimum point on an energy curve obtained by varying the common orbital exponent η of the basis. This curve is further described by Holoien as being identified with the $(2s)^2$ root of the secular equation. It is not clear on what basis this identification rests.

In the present work Holoien's CI function has been completely reproduced but not as a function belonging to a minimum point. In fact, the function was formed to belong to the point marked X on the E_3 curve in Figure 6. This point represents E = -0.7985 and η = 0.9375. Clearly that point is not a minimum of an energy curve. To further check for a possible minimum, calculations were carried out on both sides of η = 0.9375, with the results:

η = 0.9350	E_3 = -0.8006 a.u.
η = 0.9375	E_3 = -0.7985 a.u.
η = 0.9400	E_3 = -0.7967 a.u.

Clearly the trend shown by these detailed results coincide

with the gross trend shown by the E_3 curve in the neighbourhood of $\eta = 0.9375$.

There is no evidence of a minimum and therefore the present work refutes Holoien's claims for the CI function under discussion. As a consequence his rejection of the $(2s)^2\ ^1S - 1s2s\ ^1S$ transition and proposal of the $(2s)^2\ ^1S - 1s3p\ ^1P$ and $(2s)^2\ ^1S - 1s3p\ ^1P$ transitions for the corona line rest on an untenable basis.

VI.3 A CI method for the $(2s)^2\ ^1S$ state

According to the variational principle the energy of any trial function is an upper bound to the ground state energy of a system. By this same principle the energy of any trial function will be an upper bound to an excited state energy provided that function is orthogonal to the true eigen functions of all the lower states of the symmetry under consideration. Thus to obtain the best upper bound to the energy of the $(2s)^2\ ^1S$ state the trial function would have to be orthogonal to the infinitely many lower $1sns\ ^1S$ states.

This orthogonality requirement can be rephrased in terms of vector spaces. Let the trial function for the $(2s)^2\ ^1S$ state be a CI function defined as:

$$\phi_0^{(2)} = \sum_i c_{io}^{(2)}\ \phi_i^{(2)}$$

in which $\phi_i^{(2)}$ is a symmetry adapted two-electron configuration function. Then the $\phi_i^{(2)}$'s should lie completely outside the space of all 1sns ^1S state functions, that is outside the "1sns space", and should lie as much as possible in the space of all 2sns ^1S state functions, that is inside the "2sns space".

In actual variational calculations this orthogonality condition can obviously not be completely fulfilled. However, it opens the question as to what degree partial fulfilment of this condition helps to improve an upper bound to the $(2s)^2\ ^1S$ state energy. In response to this question a CI basis was selected which, firstly, should span as much of the 1sns space as possible and, secondly, should contain configuration functions lying as much as possible in the 2sns space.

The first requirement is met by the 1/n basis listed in Table 15, since, as shown earlier, this is the best basis available at present to represent the 1sns space. As for the second requirement, the success in choosing the configurations of the form 1sns in the 1/n basis to obtain CI functions for 1sns ^1S states suggests an analogous choice with respect to the 2sns space, namely the choice of configurations of the form 2sns. Thus for a first trial a 20 configuration basis was set up by adding the configurations $(2s)^2$, 2s3s, $(3s)^2$, $(4s)^2$, and

$(5s)^2$ to the 15 configurations of the 1/n basis. The new configurations, the "2sns part" of the basis, were expressed in STO's in the same way as had been done for the 1/n basis, the "1sns part" of the new basis.

The orbital exponents of the 1sns part are fixed as listed in Table 15. The orbital exponents of the 2sns part of the basis were selected to serve as a common variational parameter to be denoted by $\eta(2sns)$.

Thus by varying $\eta(2sns)$ a minimum value was sought for the 16th lowest eigen value, E_{15}, obtained by the diagonalization of the CI matrix. This eigen value is the first above the 15 eigen values corresponding to the 1sns ^1S states and is therefore expected to belong to the first 2sns ^1S state. The energy curve for E_{15} obtained by varying $\eta(2sns)$ is shown in Figure 8. The minimum value for E_{15} is -0.7338 a.u. at $\eta(2sns) = 0.925$. The complete set of E_k's obtained at $\eta = 0.925$ is listed in the fourth column of Table 21 and there compared with the E_k's earlier obtained from the 1/n basis (3rd column) and with the accurate energies (2nd column). One notes the following results:

i) the 15 E_k's belonging to the 1sns part of the basis (4th column) are all slightly lower than the corresponding values obtained with the 1/n basis alone (3rd column) and have thus improved

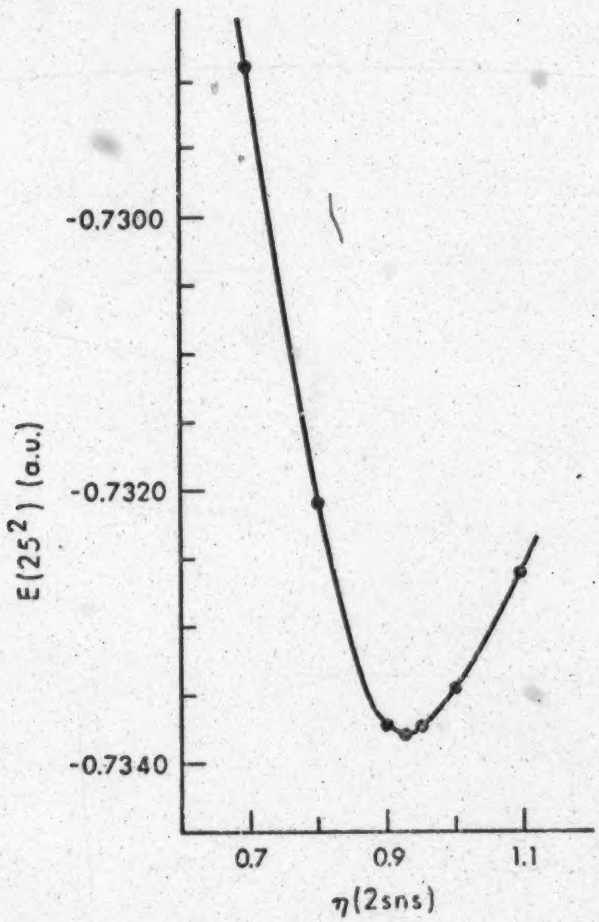

Figure 8. $E(2s^2)$ minimization.

Table 21 E_k minimization with extended 1/n basis

k	W_k (a.u.)[a]	E_k 1/n basis[b]	E_k extended basis	Coefficient of dominant RO configurations	RO occupancy
0	-2.903724	-2.875825	-2.876034	0.998236	x_1x_1
1	-2.145953	-2.142251	-2.142487	0.996584	x_1x_2
2	-2.061262	-2.059610	-2.059747	0.999098	x_1x_2
3	-2.033580	-2.032700	-2.032770	0.999642	x_1x_2
4	-2.021172	-2.020664	-2.020701	0.999826	x_1x_2
5	-2.014560	-2.014251	-2.014271	0.999905	x_1x_2
6	-2.010620	-2.010428	-2.010440	0.999943	x_1x_2
7	-2.008092	-2.007966	-2.007973	0.999963	x_1x_2
8	-2.006369	-2.006285	-2.006290	0.999975	x_1x_2
9	-2.005169	-2.005081	-2.005909	0.999982	x_1x_2
10	--	-2.004202	-2.004204	0.999987	x_1x_2
11	-2.003584	-2.003530	-2.003531	0.999990	x_1x_2
12		-2.003006	-2.003007	0.999992	x_1x_2
13		-2.002585	-2.002586	0.999991	x_1x_2
14		-1.967840	-1.971080	0.996174	x_1x_2
15			-0.733786	0.983871	x_1x_1

Table 21 (con't)

k	W_k (a.u.) [a]	E_k (b) 1/n basis	E_k extended basis	Coefficient of dominant RO configurations	RO occupancy
16			-0.579811	0.941089	x_1x_2
17			-0.358311	0.936160	x_1x_1
18			-0.115597	0.924816	x_1x_2
19			0.740578	0.939892	x_1x_2

(a) References in Table 14.

(b) Table 14.

as upper bounds to the accurate energies (2nd column).

ii) with E_{15} = -0.7338 the 2sns part of the basis does indeed establish an energy far above the series limit of -2.00 a.u. for the 1sns ^1S states.

The question remains whether E_{15} can be considered as an upper bound to the energy of the $(2s)^2\ ^1S$ state, and, if so, how dependable it may be.

First, all 20 CI functions have been submitted to an RO analysis. The coefficients of the dominant configurations are listed in the second last column of Table 21. The last column indicates whether the dominant configuration is one doubly occuped orbital (by $\chi_1\chi_2$) or has two different singly occupied orbitals (by $\chi_1\chi_2$). It is noted that for Φ_0 to Φ_{14} the pattern of the coefficients and the forms of the configurations is entirely similar to that for the original 1/n basis as shown in Table 17. Furthermore the Φ_{15} is shown having a doubly occupied RO for its dominant configuration. This is strong support for interpreting Φ_{15} as being an approximation to the $(2s)^2\ ^1S$ state. It also strengthens the expectation that the present approach represents a substantial step towards a viable CI method for doubly excited ^1S states.

A second analysis of the data dealt with the question

to what extent the lsns part of the basis represents a convergence towards a complete spanning of the lsns space, defined above. The better this convergence the more stable the lsns part of the basis can be considered in the sense that the removal of one lsns configuration should not appreciably change the lowest doubly excited state energy, $E(2s^2)$. To test this stability, a number of calculations were performed in which the lsns part of the basis was reduced by omitting, one at a time, the configurations 1s15s, 1s14s, ... 1s7s in that order.

In Table 22 are listed the values for $E(2s^2)$ obtained after each reduction of the basis together with the coefficients of the corresponding dominant RO configuration. The dominant configuration retains its doubly occupied character throughout the reduction of the basis.

To show the trend of the $E(2s^2)$ values and the dominant coefficients a plot is given in Figure 9. The curves clearly show a degree of convergence toward a limiting value for both $E(2s^2)$ and the dominant coefficient.

Further evidence of the stability of the lsns part of the basis is obtained from following the changes in the E_k values as the reduction of the basis progresses.

Table 22 Progressive Reduction of the CI basis

Configurations Removed	$E(2s^2)$	Coefficient RO Analysis
	-0.7337	0.9839
1s15s	-0.7347	0.9824
+1s14s	-0.7356	0.9809
+1s13s	-0.7367	0.9792
+1s12s	-0.7380	0.9770
+1s11s	-0.7397	0.9743
+1s10s	-0.7419	0.9708
+1s9s	-0.7448	0.9662
+1s8s	-0.7488	0.9603
+1s7s	-0.7547	-0.9525
+1s6s	-0.7639	-0.9428
+1s5s	-0.7793	-0.9325

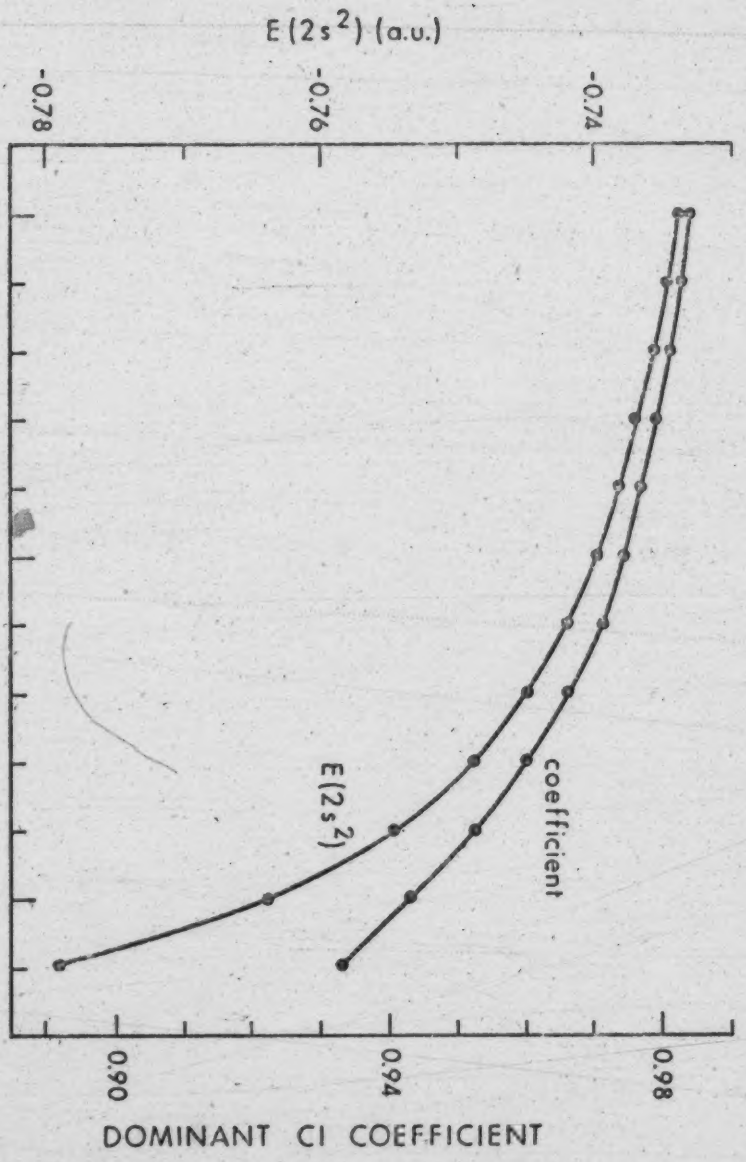

Figure 9. Reduction of isns part of CI basis.

In Table 23 some examples are given which are representative of the overall trend throughout the reduction of the basis. The table has been organized to show the surprising fact that, as the basis is reduced by one configuration, the eigen value removed is not the uppermost of the lsns part but rather the second highest. That uppermost lsns eigen value remains in the neighbourhood of -2 a.u., the series limit of the lsns ^1S energies.

The last column lists each E_k value reached before it was removed by reduction of the basis. Excepting the two highest E_k values the largest differences between the initial values (first column) and the final values (last column) occur in the third decimals. Thus the E_k values belonging to the lsns part of the basis show a remarkable stability throughout the reduction of the basis.

Although further work could be done on optimization of the lsns part of the basis and on inclusion, in the 2sns part, of more functions to improve the radial and angular correlation, the present work is adequate to the purpose of determining whether the $(2s)^2\ ^1S$ state is the upper state of the 279,715 cm^{-1} corona line. The correlation energy of the ground state of He is close to 0.03 a.u. (30). This must be less for the

Table 23 E_k's from reduced bases

Initial E_k's	E_k's after removal of 1s15s	1s15s...1s12s	1s15s...1s8s	Final E_k's
-2.876034	-2.876034	-2.876034	-2.876033	-2.876026
-2.142487	-2.142472	-2.142425	-2.142329	-2.142208
-2.059747	-2.059719	-2.059622	-2.059358	-2.058713
-2.032770	-2.032741	-2.032635	-2.032263	-2.031516
-2.014271	-2.014252	-2.014171	-2.013581	-2.013581
-2.010440	-2.010426	-2.010358		-2.010017
-2.007973	-2.007962	-2.007904		-2.007725
-2.006290	-2.006283	-2.006220		-2.006150
-2.005090	-2.005085	-2.005015		-2.005015
-2.004204	-2.004201			-2.004168
-2.003531	-2.003529			-2.003516
-2.003007	-2.003002			-2.003002
-2.002586				-2.002586
-1.971080	-1.973716	-1.981866	-1.99443	-2.029508
-0.733786	-0.734700	-0.738037	-0.748822	-0.779288

$(2s)^2\ ^1S$ state since the electron probability density is more diffuse in the $(2s)^2\ ^1S$ state than in the ground state. Therefore the value of -0.7338 a.u., obtained for the $(2s)^2\ ^1S$ state, cannot be expected to be lowered by more than 0.03 a.u. Thus the true energy of the $(2s)^2\ ^1S$ state must lie between -0.704 and -0.734 a.u. according to the present work. It was, however, calculated above that this energy should be -0.8716 a.u. if the $(2s)^2\ ^1S$ state was the upper state of the corona line. It is therefore concluded that the corona line at 279,715 cm^{-1} is not due to a $(2s)^2\ ^1S$ - $1s2s\ ^1S$ transition.

BIBLIOGRAPHY

1. J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).
2. L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics, McGraw-Hill Co., New York (1935)
3. F. L. Pilar, Elementary Quantum Chemistry, McGraw-Hill Co., New York (1968).
4. A. W. Weiss, Phys. Rev. 122, 1826 (1961).
5. C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3348 (1972).
6. R. P. Messmer, Theoret. Chim. Acta (Berl.) 14, 319 (1969).
7. J. H. Choi, C. F. Lebeda and R. P. Messmer, Chem. Phys. Letters, 5, 503 (1970).
8. U. Liebe, Wave Functions of Excited Atoms, Ph.D. Thesis, University of Alberta, Edmonton, Canada. Spring, 1972.
9. E. Holoien, Phys. Rev. 104, 1301 (1956).
10. A. W. WEiss, Phys. Rev. 122, 1826 (1961).
11. C. E. Eckart, Phys. Rev. 36, 878 (1930).
12. Y. Accad, C. L. Pekeris and B. Schiff, Phys. Rev. A4 516 (1971).
13. H. M. James and A. S. Coolidge, Phys. Rev. 51, 860 (1937).
14. H. Preuss, Theoret. Chim. Acta (Berl.) 2, 98 (1964).
15. P. S. C. Wang and F. Weinhold, J. Chem. Phys. 57, 1738 (1972).

16. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, 1967.

17. C. E. Moore, Atomic Energy Levels, Circular 467 of the U.S. National Bureau of Standards, 1952.

18. Per-Olav Lowdin and Harrison Shull, Phys. Rev. 101, 1730 (1956).

19. F. W. Birss, private communication.

20. J. C. Slater, Quantum Theory of Atomic Structure, Volume II, McGraw-Hill Co., New York (1960), p. 40.

21. F. W. Birss, Computing Science 450, 1971, p. 263-265.

22. J. H. Wilkinson, The Algebraic Eigen value Problem, Clarendon Press, Oxford, 1965.

23. A. L. Stewart, Adv. Phys. 12, 299 (1963).

24. C. L. Pekeris, Phys. Rev. 127, 509 (1962).

25. J. C. Slater, Quantum Theory of Atomic Structure, Volume I, McGraw-Hill Co., New York (1960), p. 112-114.

26. E. Holoien, Proc. Phys. Soc. 71, 357 (1958).

27. K. T. Compton and J. C. Boyce, J. Franklin Inst. 205, 497 (1928).

28. F. G. Kruger, Phys. Rev. 36, 853 (1930).

29. B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. A, 66, 904, 911 (1953).

30. E. Clementi, Tables of Atomic Functions, IBM Corporation, San Jose, California, 1965.